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FY 2002

**Progress Report for Fuels for Advanced Compression
Ignition Direct Injection (CIDI) Engines**

**Energy Efficiency and Renewable Energy
Office of FreedomCAR and Vehicle Technologies**

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I. INTRODUCTION

Enabling Advanced Vehicle Technologies through Development and Utilization of Advanced Petroleum-Based and Renewable Fuels



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On behalf of the Department of Energy's Office of FreedomCAR and Vehicle Technologies (FCVT), we are pleased to introduce the Fiscal Year (FY) 2002 Annual Progress Report for the Fuels for Advanced Compression Ignition Direct Injection (CIDI) Engines Activity which is part of the Fuels Technologies Program. Together with DOE National Laboratories and in partnership with private industry and universities across the United States, FCVT engages in high risk R&D that provides enabling technology for fuel efficient and environment-friendly vehicles. This Activity is currently focused on advanced fuels for the CIDI engine, an advanced version of the commonly known diesel engine, which is used in both light- and heavy-duty vehicles.

Since its inception, the Fuels for Advanced CIDI Engines Activity has supported the FreedomCAR government/industry partnership through its technology research projects. The work in advanced petroleum-based fuels is conducted through joint programs with the energy and automotive industries. Advanced petroleum-based fuels will also be necessary for the 21st Century Truck Initiative that proposes to triple medium-duty truck fuel economy and double heavy-duty truck fuel economy on a ton-mile per gallon basis to meet its goals. In FY 2002, the focus of our research activities was on developing and testing selected advanced fuels in combination with near-term emission control technologies in CIDI engines. The Fuels for Advanced CIDI Engines Activity works closely with the Combustion and Emission Control R&D Program for Advanced CIDI Engines to assure that the advanced fuels work facilitates development of emission control technologies that will maintain the high fuel efficiency of CIDI engines while meeting future emission standards.



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This report highlights progress achieved during FY 2002 and comprises 18 summaries of industry and National Laboratory projects that were conducted. It provides an overview of the exciting work being conducted to tackle the tough technical challenges associated with developing clean-burning fuels that will enable meeting the performance goals of the Emission Control R&D Program for Advanced CIDI Engines. The summaries cover the effects of fuels on CIDI engine emissions; the effects of lubricants on engine emissions; the effects of fuels and consumed lubricants on exhaust emission control devices; and the health and safety, materials compatibility, and economics of advanced petroleum-based fuels. A brief snapshot of FY 2002 accomplishments and new directions for FY 2003 is captured on the following pages. We are encouraged by the technical progress realized in FY 2002 and look forward to making further advancements in FY 2003.

Advanced petroleum-based fuels are a critical enabler to allow the high fuel economy of diesel-powered vehicles to be maintained while meeting future

emission standards. Through this research, the Fuels for Advanced CIDI Engines Activity will identify the most suitable fuels for the advanced CIDI engines that power these vehicles. Sulfur content is a very important issue for the Fuels for Advanced CIDI Engines Activity. The most desirable emission control devices for nitrogen oxides (NO_x) are deactivated by sulfur in currently available fuels. Results from the Fuels for Advanced CIDI Engines Activity were a primary source of information used by the U.S. Environmental Protection Agency (EPA) to establish new diesel fuel sulfur content standards (i.e., 15 ppm maximum) beginning in 2006.

On July 30, 2001, EPA Administrator Christine Whitman announced that EPA would request an independent review of the 2007 heavy-duty diesel engine emissions standards and the diesel fuel sulfur content standard to provide "advice to the EPA on technology issues associated with the introduction of technology to reduce engine exhaust emissions and technology to lower the sulfur level of highway diesel fuel in accordance with the dates incorporated in the highway diesel program promulgated in 2001." The Clean Diesel Independent Review Panel was thus created to carry out this review. The specific objectives of the panel's charter were to assess the progress of:

- manufacturers of diesel engines and emission control systems in developing technology to reduce engine exhaust pollutants, and;
- the fuels industry in developing and demonstrating technologies to effectively lower the sulfur level of highway diesel fuel.

The panel was composed of leading experts from the public health community, petroleum refiners, fuel distributors and marketers, engine manufacturers, emission control systems manufacturers, and state governments. In their final report, the Panel found that NO_x adsorbers and catalyzed particulate filter systems are the two leading emission control technologies for diesel engines. They also identified that improving the durability of the NO_x adsorber, especially as it relates to desulfation (removing accumulated sulfur), is the most significant fundamental challenge that is being addressed currently. These findings directly support the research priorities of the Fuels for Advanced CIDI Engines Activity.

A major component of the Fuels for Advanced CIDI Engines Activity is the Advanced Petroleum-Based Fuels - Diesel Emission Control project (APBF-DEC). The APBF-DEC is an industry/government project to identify and evaluate: (1) the optimal combinations of low-sulfur diesel fuels, lubricants, diesel engines, and emission control systems to achieve ultra-low NO_x and particulate matter (PM) emissions for the 2001 to 2010 time period; and (2) properties of fuels and vehicle systems that could lead to even lower emissions beyond 2010. The activities being conducted under the APBF-DEC project include both light-duty and heavy-duty CIDI engines. A systems approach is being used, i.e., simultaneously investigating fuels, lubricants, engines, and emissions control systems. A government/industry steering committee and working groups are guiding the APBF-DEC project.

The co-operative projects being conducted with the Ad-Hoc Auto/Energy Working Group comprise another important component of the Fuels for Advanced CIDI Engines Activity. Phase I of the Ad-Hoc program looked at engine-out emissions of a diesel fuel with dimethoxy methane, an oxygenated diesel fuel



Automobiles	Government	Emission Control	Energy/ Additives
Ford	DOE	NIKA	API
GM	NREL	Johansen/Mattney	American Chemistry Council
DaimlerChrysler	ORNL	Dubicki	BP
Toyota	EPA	3M	Edyl
	CARB/SCAQMD	Engelhard	ExxonMobil
		Siemens	Marathon Ashland
		Bentler	Pennzoil/Quaker State
		ArvinMeritor	Lubrizol
		Clean Diesel Tech.	Equilon
		Corning	Texaco
		Donaldson Co.	Chevron/Dreosite
		GM	Clia
		IGR	Chevron Products
		Isodia	Esso
		Tenneco Automotive	Valvoline
			Motiva
			Infinium

APBF-DEC Participants

additive. The results from this study showed that this oxygenated fuel additive significantly lowered PM and poly-aromatic hydrocarbon (PAH) emissions compared to the base diesel fuel, and its emissions were essentially equivalent to a Fisher-Tropsch fuel. In Phase II, a new set of fuels will be evaluated, including different oxygenates blended in refinery produced low-sulfur fuels. The goal of Phase II is to determine the impact these fuels have on the physical and chemical characterization of PM after an oxidation catalyst and a diesel particulate filter.

SIGNIFICANT FY 2002 ACCOMPLISHMENTS

In FY 2002, much effort continued on the determination of the effects of fuel sulfur content on CIDI NO_x and PM emission control devices. From this work, preliminary findings indicate that NO_x emission control devices currently do not have sufficient durability to last the full useful life of the vehicle due to sulfur contamination from the combined contributions of 15 ppm sulfur fuel and consumed lubricating oil. Future work will focus on quantifying the effect of sulfur (from the fuel and lubricating oil) on emission control device durability, and the need for sulfur traps and development of desulfurization strategies to attain full useful life operation.

Southwest Research Institute showed that oxygenates can improve the EGR tolerance of CIDI engines resulting in significant NO_x and PM emission reductions with potential to meet "fuel reformulation" targets. Environmental assessments of two of the most promising diesel fuel oxygenates, dibutyl maleate and tripropylene glycol monomethyl ether, were completed by Lawrence Livermore National Laboratory (LLNL). In tests using these same two oxygenates, Sandia National Laboratories (SNL) found through laser imaging that these oxygenates also affect the injected fuel spray patterns with further beneficial effects on PM emissions. LLNL made improvements in their new measurement technique to determine the origin of PM from CIDI engines, from the components of both the fuel and lubricating oil. Another highlight was the data collected by NREL showing that ultra-low sulfur diesel fuel and catalyzed PM traps can reduce HC, CO, and PM by 91 to 99%.

In July 2002, the National Renewable Energy Laboratory (NREL) established the Renewable Fuels and Lubricants (ReFUEL) Research Laboratory, a high-altitude facility for testing alternative and advanced fuels and heavy-duty engines and vehicles. ReFUEL is the first laboratory in the United States dedicated to researching and developing renewable and synthetic fuels and lubricants for heavy-duty transportation applications. It's also the only laboratory to evaluate the effects of operating heavy-duty vehicles at high altitude. The laboratory houses the following specialized testing and measurement equipment:

- Chassis dynamometer for developing advanced trucks and buses
- Engine test cell for fuels R&D
- Emissions analysis lab for measuring and understanding emissions.

The ReFUEL Research Laboratory will be used to support various "working group" projects, which were developed in response to the needs outlined by groups of government and industry personnel:

- Advanced Petroleum-Based Fuels Project - Identifying optimal combinations of fuels, lubricants, diesel engines, and emission control systems for reducing emissions.
- EC-Diesel Technology Validation Project - Evaluating an ultra-low sulfur fuel and particulate matter after-treatment.
- Fischer-Tropsch Synthetic Fuel Demonstration - Investigating the characteristics of Fischer-Tropsch synthetic diesel fuel.
- Next Generation Natural Gas Vehicle Project - Working with industry to develop commercially viable medium- and heavy-duty natural gas vehicles.

The following brief summaries list the highlights of research and testing conducted in the Fuels for Advanced CIDI Engines Activity during FY 2002.

APBF-DEC Project Progress

APBF-DEC currently directs five individual projects: Effects of Lubricant Composition on Emissions; Effects of Fuel Composition on Selective Catalytic Reduction (SCR) and Diesel Particulate Filters (DPF) Systems; and the Effects of Fuel Composition on NO_x Adsorber/DPF Systems (three separate projects).

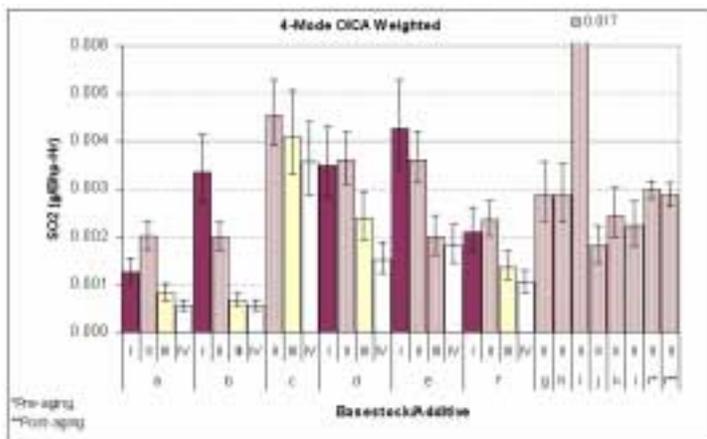
The APBF-DEC projects are timely because of the stricter emissions standards mandated by EPA. Between 2004 and 2009, lower emissions standards will be phased in for passenger cars and light-duty trucks. For diesel-powered vehicles to comply with these standards, catalytic emission control systems will be required. EPA has also set new emission standards for heavy-duty engines, which will go into effect in 2007, and a standard for the sulfur content in highway diesel fuel slated to go into effect in 2006. These standards (for emissions of both PM and NO_x) will require catalytic emission control systems on heavy-duty vehicles.

The following provides updates of progress for each of the APBF-DEC projects over the past year.

Effects of Lubricant Composition on Emissions

The Diesel Emission Control - Sulfur Effects project (<http://www.ott.doe.gov/decse/>) quantified the impact of diesel fuel sulfur on the performance and short-term durability of diesel emission control devices. The acute sensitivity of certain of these devices highlighted the need to study another source of sulfur and other potential poisons - specifically the diesel lubricating oil.

To address this concern, a research project to study lubricant formulation (basestocks and additives) effects on diesel emission control systems is entering its second year. It is anticipated that the results of this study will be critical in defining the needs of future lubricant formulations for both light-duty and heavy-duty diesel engines. An International T444E (7.3L, V8) has been installed in an emissions test cell and has been upfit with exhaust gas recirculation (EGR) and closed crankcase ventilation (CCV) hardware similar to future base engine designs. During the past year, test lubricants ranging in sulfur content between 0 and 6500 parts per million (ppm) and ash between 0% and 1.85% have been prepared in four basestocks - one each from the four major base oil classifications (Group I-IV) as defined by the American Petroleum Institute (API). All Phase I testing, including 12 additives and four basestocks, has been completed. In the coming year, the influence of the lubricant derived emission components on catalyst durability will be examined, and a rapid aging protocol to accelerate lubricant effects testing will be developed and utilized to determine if consumed diesel engine oil impacts catalyst life.



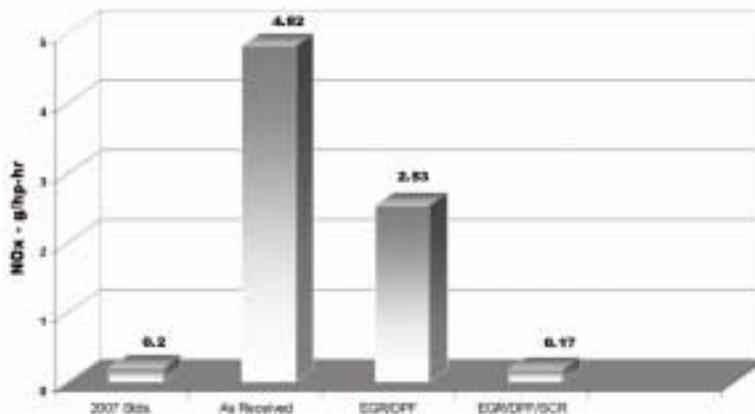
SO₂ Emissions for the Various Oils Tested

Effects of Fuel Composition on SCR/DPF Systems

The overall objective of this project is to demonstrate the low-emissions performance of advanced diesel engines operating on advanced fuels, and equipped with low-pressure-loop EGR plus urea SCR and DPF. During the past year, a Caterpillar C-12 engine was installed in an emissions test cell and tested in its as-

received configuration with D2 diesel fuel containing 350 ppm sulfur. Emissions results for the baseline over the U.S. heavy-duty transient cycle were ~ 3.55 g/hp-hr NO_x and ~ 0.065 g/hp-hr PM. Results over the steady-state European OICA cycle were 4.82 g/hp-hr NO_x and 0.031 g/hp-hr PM. The engine was fitted with a low-pressure-loop cooled EGR system provided by STT-Emtech in Sweden and a diesel particulate filter (part of System A) provided by the Manufacturers of Emissions Control Association (MECA), and the systems were optimized for low engine-out NO_x.

Engine-out NO_x over the transient cycle with the EGR system using 3-ppm sulfur fuel was reduced to 1.5 g/hp-hr (58%). Over the steady-state OICA cycle, NO_x emissions were reduced to 2.32 g/hp-hr (52%). Particulate emissions for both tests remained below 0.01 g/bhp-hr. The urea SCR catalyst of System A was added to the emission control system along with urea injection systems provided by Robert Bosch, and the calibration of the SCR system for NO_x reductions was engineered. Results on the steady-state OICA test showed tailpipe NO_x reduced to only 0.17 g/hp-hr (96%). The calibration is being optimized at this time for testing over the transient cycle. Then, a matrix of emission tests with the different fuels will be carried out before the system is installed on one of the durability engines for the beginning of the 6,000-hour durability test.



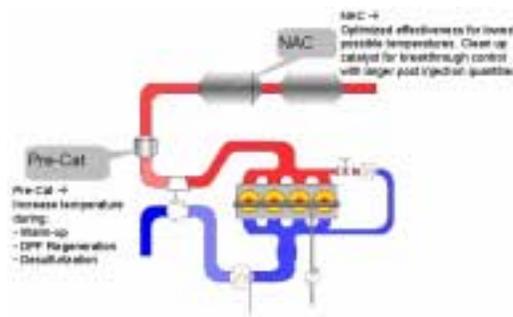
Progression of NO_x Emission Reductions

Effects of Fuel Composition on NO_x Adsorber/DPF Systems

The overall objective of these projects is to demonstrate the potential of NO_x adsorber technology in combination with diesel particulate filters, advanced fuels, and advanced engine controls to achieve stringent emission levels while maintaining high fuel economy in light-duty cars and trucks and heavy-duty engines. The goal for the light-duty projects is to achieve stringent Tier 2 Bin 5 light-duty emission standards with limits of 0.07 g/mi NO_x and 0.01 g/mi PM. The goal for the heavy-duty engine is to achieve the stringent 2007 standards of 0.2 g/bhp-hr NO_x and 0.01 g/bhp-hr PM. In addition, these projects intend to determine the necessary fuel sulfur level and other fuel properties that will enable these systems. The fuel sulfur levels tested will be representative of those required to be available beginning June 2006 (<15 ppm S).

• Passenger Car Engine/Vehicle

A model year 2001 Audi A4 Avant with a 1.9 liter TDI engine (100 KW at 4,000 rpm) with a Bosch common rail second generation fuel injection system, integrated EGR and a Garrett GT 17 V turbine was acquired as the test vehicle for this project. Two additional engines were acquired and installed in emissions test cells. The emission control system (ECS) architecture was designed, and exhaust system modifications were completed. An integrated external electronic controller was installed to control post injection and lean and rich cycling conditions necessary for catalyst regeneration. Rapid warm-up procedures, other thermal management approaches, and protocols for sampling and analysis of unregulated toxic emissions were developed. ECS system regeneration and desulfurization



Schematic of Passenger Car Emission Control System

strategies were devised. A limited amount of baseline and engine-out data has been collected. Aging and evaluations testing will generate a significant body of data in FY 2003.

- **Light Truck Engine/Vehicle**

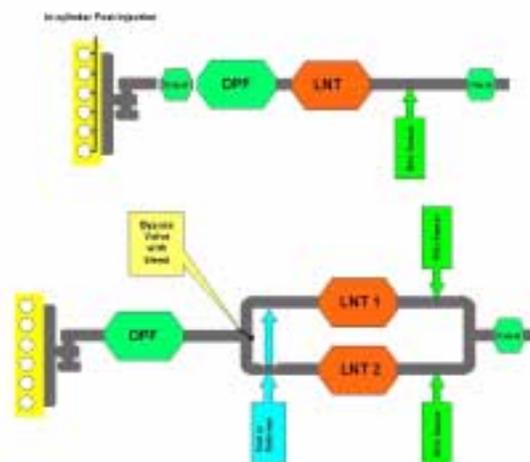
A model year 2002 Chevrolet 2500 Series Silverado with a 6.6 liter Duramax engine (300 HP at 3100 rpm) with a Bosch common rail fuel injection system, integrated exhaust gas recirculation (EGR), charge air cooler, and a center mounted turbine was acquired as the test vehicle for this project. In order to make the objectives of this project possible and limit the reduction efficiencies required by the aftertreatment devices, significant modifications have been made to the test engine to lower engine-out emissions. These include installation of low pressure EGR, a turbo by-pass system, and engine calibration changes (for lower engine-out NO_x and more favorable exhaust temperature profiles). In addition, secondary injection and dual wall insulated exhaust components will be used to retain heat for the ECS. A limited amount of baseline and engine-out data has been collected. Aging and evaluations testing will generate a significant body of data in FY 2003.



6.6 liter Duramax Engine

- **Heavy-Duty Engine**

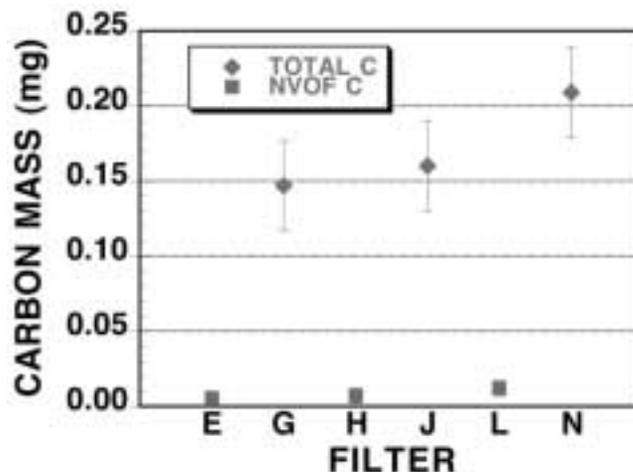
A 15L Cummins ISX 500 hp inline, 6-cylinder heavy-duty diesel engine has been installed for testing. This engine has dual overhead camshafts and is equipped with integrated EGR and a variable geometry turbocharger (VGT) and is calibrated to meet the 2004 heavy-duty (HD) emission standards (2.5 g/bhp-hr NO_x , 0.1 g/bhp-hr PM). Modifications made for testing include: installation of secondary in-cylinder fuel injectors and engine calibration changes (for lower engine-out NO_x and more favorable exhaust temperature profiles). Preliminary results indicate that the NO_x adsorber catalyst can reduce NO_x emissions by 85% and, at peak efficiency, by up to 98%. Early results also show NO_x emissions can be reduced to 0.10-0.20 g/bhp-hr, nearing the 2007 targets. However, HC emissions were high (1.4 g/bhp-hr), and the associated fuel economy penalty is greater than desired (10%). Optimization of the rich regeneration strategy and addition of a downstream diesel oxidation catalyst (DOC) is required to minimize hydrocarbon (HC) slip. The back pressure associated with the emission control devices has prohibited operating at high load conditions. Cycling the engine from lean to rich places additional demands on the engine, turbocharger, and EGR system, so durability effects on the engine may need to be evaluated further. Aging and evaluations testing will generate a significant body of data in FY 2003.



Single and Dual Leg Emission Control Systems are Being Tested

LLNL Refines Technique to Trace the Origin of Emissions from Fuel Composition

Regulatory pressure to significantly reduce the particulate emissions from diesel engines is driving research into understanding mechanisms of soot formation. If mechanisms are understood, then combustion modeling can be used to evaluate possible changes in fuel formulation and suggest possible fuel components that can improve combustion and reduce PM emissions. The combustion paradigm assumes that large molecules break down into small components and then build up again during soot formation. Lawrence Livermore National Laboratory (LLNL) has applied accelerator mass spectrometry (AMS) to fuel combustion in engines. AMS allows labeling specific carbon atoms in fuel components, including oxygenates, tracing the carbon atoms, and directly measuring how fuel molecular structure affects emissions. Volatile and non-volatile organic fractions (VOF, NVOF) in the PM can be further separated. The effectiveness of exhaust stream catalysts to oxidize products from tracer fuel components can be monitored through AMS measurement of carbon in PM. The data collected during the past year provide direct validation of chemical kinetic models. Using this information, the PM-producing tendencies of fuels can be predicted without doing extensive and expensive engine testing. It will also provide information on the types of fuel structures that best reduce formation of PM.

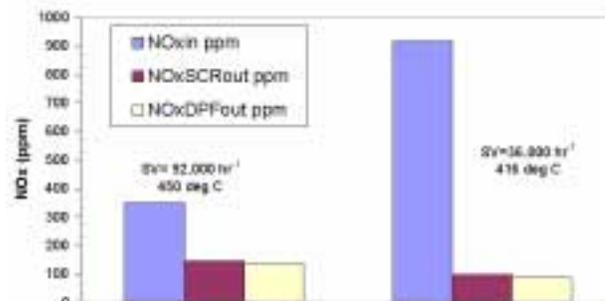


Measurements of Total Carbon and the Non-Volatile Organic Fraction

ORNL Explores Unregulated Emissions from Urea SCR Emission Control Systems

Urea selective catalytic reduction (SCR) has emerged as a promising technology for the reduction of NO_x from CIDI engines. Several groups have demonstrated emissions levels at or near the EPA 2007 HD standards as well as Tier 2 levels for light-duty vehicles. The technology uses a urea solution injected into the exhaust as a source of ammonia, which then reacts with NO_x on the catalyst to reduce NO_x to N₂. In an ideal case, the urea dissociates completely in the exhaust to ammonia and CO₂. However, many other urea decomposition products are possible.

These and other unregulated emissions, such as NH₃ and N₂O, are important to characterize both for potential health effects issues as well as an indicator of catalyst system performance. Unregulated emissions were collected during this preliminary phase of the research. Impinger samples showed an excess of cyanic acid being generated during several of the modes which is believed to be due to excess urea solution being injected. While the preliminary results were unusual due to the excess of urea injected, the methods developed for unregulated emissions analysis worked very well, and much better success in subsequent experiments with a properly functioning urea injection system is anticipated. Further work will focus on testing of two SCR formulations and two fuels. Because of the unusual results with excess urea injection, it is planned to study

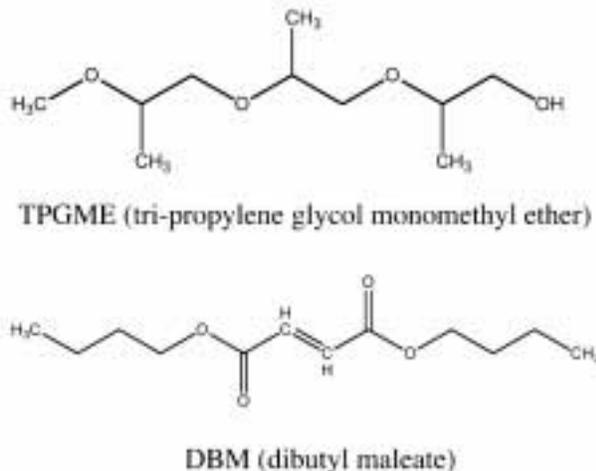


NO_x Reduction Effectiveness at Two Operating Conditions

more mild excursions from normal operation. An important finding from this work will be to define the threshold to the excess urea injection above which the unusual chemistry occurs.

LLNL Studies the Impact of Oxygenated Blending Compounds on PM and NO_x Formation of Diesel Fuel Blends

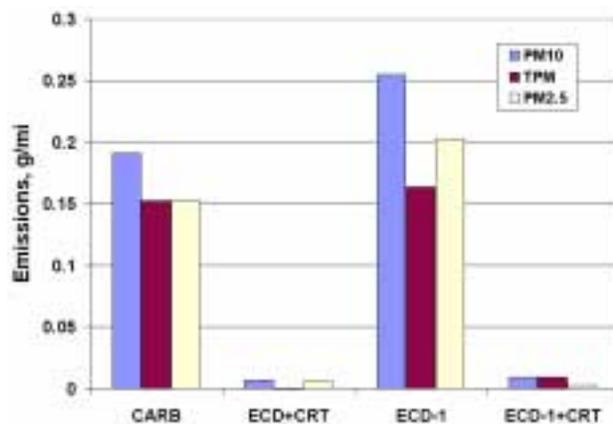
Chemical kinetic modeling has been developed uniquely at Lawrence Livermore National Laboratory (LLNL) to investigate combustion of hydrocarbon fuels in practical combustion systems such as diesel engines. Experimental diesel engine studies have indicated that when oxygen is added to diesel fuel, soot production in the engine is reduced. The soot reduction appears to be largely independent of the way oxygen is incorporated into the reactants, whether through entrainment of additional air into the reacting gases or direct inclusion of oxygen atoms into the diesel fuel molecules. During the past year, LLNL examined dibutyl maleate (DBM) and tripropylene glycol monomethyl ether (TPGME), both of which include significant amounts of oxygen imbedded in the primarily hydrocarbon fuel molecule. Detailed chemical kinetic reaction mechanisms were developed for both of these fuels, and the resulting models were used to assess their sooting tendencies. The model calculations indicate that the distribution of oxygen atoms within the fuel molecule can have a significant influence on the anti-sooting effects of the oxygen atoms. TPGME is an excellent example of such a fuel. Ongoing kinetic analyses are examining the implications of these results and may lead to new definitions of potentially important diesel fuels for engine combustion.



Chemical Structure of TPGME and DBM

NREL Tests Heavy-Duty Vehicles after Using EC-Diesel and PM Filters for One Year

ARCO, a BP company, has developed two new diesel fuels called Emission Control Diesel (ECD) and Emission Control Diesel-1 (ECD-1). Both fuels have sulfur content less than 15 ppm. The ECD fuel has an aromatics content of 10% and a cetane number of 60. The ECD-1 fuel, BP's commercial product, has an aromatics content of 22% and a cetane number of 50. Catalyzed diesel particle filters have been shown to operate more efficiently as diesel fuel sulfur content is decreased. Ultra-low sulfur diesel fuels expand the filter regeneration temperature window, improving particulate matter removal for a wide range of engine operating conditions. A one-year technology validation project was conducted to evaluate ECD and catalyzed diesel particle filters on diesel vehicle fleets in Southern California. The fuel's performance, impact on engine durability and vehicle performance, and emission characteristics were evaluated and compared to conventional California Air Resources Board (CARB) specification diesel fuel. Two rounds of emissions testing have been completed, showing that the filters are

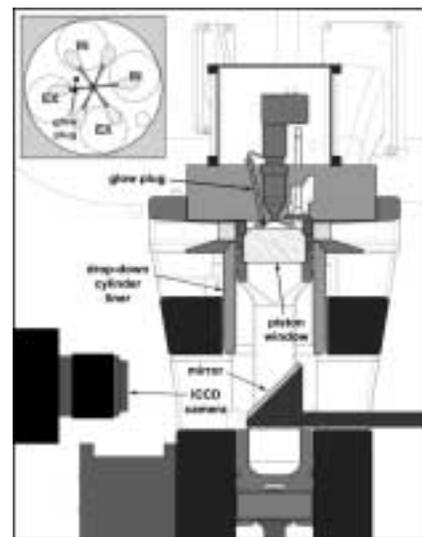


Emission Reductions Using ECD-1 Fuel and Catalyzed PM Filters

effective at removing PM, HC, and CO emissions after twelve months of continuous use. Vehicles operating on ECD with the filters did not have a significant fuel economy penalty compared to vehicles operating on conventional diesel fuel. The filters were effective at reducing unregulated emissions, such as PM10, PM2.5, and light olefins.

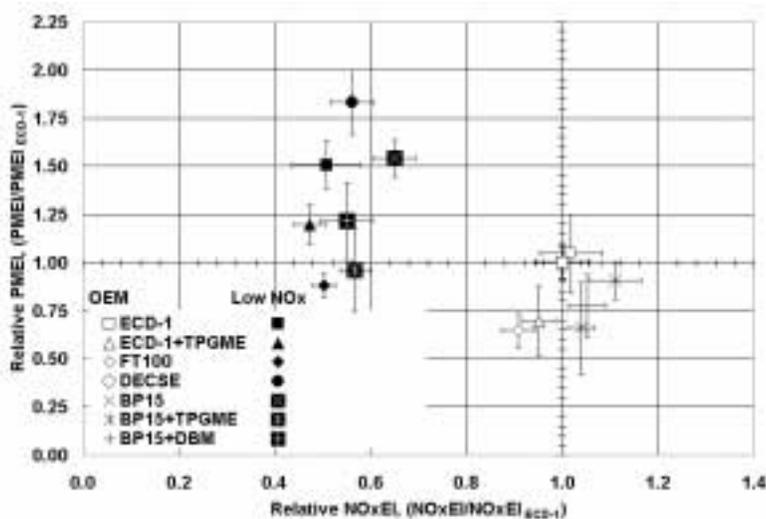
SNL Investigates Combustion Characteristics of Advanced Diesel Fuels

Blending oxygen-containing compounds ("oxygenates") with diesel fuel can lead to reduced soot and NO_x emissions, as well as reduced fuel consumption. The detailed mechanisms that cause such reductions are not well understood. SNL used spatially integrated natural luminosity (SINL) as a means to estimate in-cylinder soot concentrations. They found that the relative amount of soot produced decreases as the oxygen content of the fuel increases. Two promising oxygenated fuels were tested, and one oxygenated fuel was found to be more effective at reducing soot than the other, even though their oxygen content, combustion phasing, adiabatic flame temperature, and engine operating conditions were matched. Two possible explanations for the difference observed are differences in air entrainment and differences in molecular-structure/chemical characteristics of the fuels. Experiments using accelerator mass spectrometry diagnostics are currently underway to test this hypothesis and to identify improved oxygenate molecules for PM reductions.



SwRI Explores Toxic Emissions from Advanced CIDI Engines and Fuels

The control of NO_x emissions is probably the greatest technical challenge in meeting future emission regulations for diesel engines. In this project, lowering engine-out emissions of NO_x by increasing EGR and retarding timing will likely cause an increase in PM emissions. In Phase I of this project, it was shown that the use of an oxygenated diesel fuel additive will lower PM emissions. Use of an oxygenated diesel fuel additive thereby can minimize the increase in PM emissions that accompany the techniques used to decrease NO_x emissions. The overall objective of this project is to better understand the effects of fuels and emission control devices on the exhaust emissions of a subset of potentially toxicologically relevant compounds from an engine operated to minimize NO_x emissions. Testing confirmed that oxygenated diesel fuels and Fischer-Tropsch diesel fuels made from natural gas have greater capacity to reduce NO_x emissions without increasing PM emissions. Investigation of the role of fuels in reducing tailpipe exhaust emissions of potentially toxicologically relevant compounds, utilizing a diesel oxidation catalyst and a catalyzed particulate filter, will be starting in late FY 2002.



NO_x and PM Emissions for the Fuels Tested

The Consortium for Fossil Fuel Science (CFFS) Researches Production of Clean Liquid Transportation Fuels from Natural Gas

The Consortium for Fossil Fuel Science (CFFS) is a research consortium with participants from five universities - the University of Kentucky, University of Pittsburgh, University of Utah, West Virginia University, and Auburn University. The CFFS universities are collaborating in a research program to develop C1 chemistry processes to produce clean transportation fuel from resources such as coal and natural gas, which are more plentiful domestically than petroleum. The processes under development will convert feedstocks containing one carbon atom per molecular unit into ultra clean liquid transportation fuels (gasoline, diesel, and jet fuel) and hydrogen, which many believe will be the transportation fuel of the future. The feedstocks include syngas, a mixture of carbon monoxide and hydrogen produced by coal gasification or reforming of natural gas; methane; methanol; carbon dioxide; and carbon monoxide. During the past year, CFFS research has discovered that small (~1%) additions of probe molecules with carbon-carbon triple bonds dramatically enhance the presence of oxygenated products in Fischer-Tropsch diesel fuel which assist in reducing PM emissions. In addition, CFFS has developed Pt/W/ZrO₂ catalysts that are very effective at increasing the yield of Fischer-Tropsch diesel fuel by converting the waxes that are co-produced.

Honeywell Initiates Development of an Onboard Fuel Sulfur Trap

The objective of this project is to demonstrate at the pilot scale level proof-of-concept for a fuel desulfurization filter that is able to reduce sulfur levels in the fuel to tolerable levels which enable the implementation of post-combustion NO_x adsorber technology. A sulfur removal device can expedite implementation of new emission control systems by reducing the need for diesel fuels to attain ultra low sulfur levels. It is anticipated the cost of the proposed sulfur-removal device to the consumer will represent no more than a low multiple of the current cost of a standard fuel filter. This project began in April 2002. Representative fuel samples have been prepared, and sufficient quantities of these are now in place to begin the experimental stage of the project. Analytical procedures have been put in place for measuring total sulfur and speciation of the sulfur contaminants.

FUTURE INITIATIVES

Our new initiatives for FY 2003 build upon the progress made in FY 2002 and will focus on those areas that industry agrees are major technical barriers.

- **Honeywell On-Board Desulfurization Fuel Filter:** Honeywell will survey all applicable current and proposed approaches to fuel desulfurization and rank those suitable for on-board filtering. Following the down-select of potential technologies, laboratory screening of them will be conducted prior to prototype development and on-vehicle demonstration.
- **Advanced Petroleum-Based Fuels - Diesel Emissions Control:** APBF-DEC projects are anticipated to complete the activities described in the following:

Effects of Lubricant Composition on Emissions: It will be determined to what extent lubricant related emissions species impact the performance and durability of emissions control devices designed to reduce NO_x and PM emissions from diesel engines. A protocol for rapidly aging emission control devices and determining lubricant effects will be developed. This test protocol will then be utilized to determine if lubricant sulfur, ash, and certain metals need to be controlled to meet useful life standards placed on emission control systems.

Effects of Fuel Composition on SCR/DPF Systems: Emissions testing using System A will be completed, and the emissions tests with the fuels matrix will be carried out. Following that, System A will be moved to the durability test cell while work will begin on System B to optimize and calibrate that system for minimum emissions.

Effects of Fuel Composition on NO_x Adsorber/DPF Systems: All three projects (Passenger Car Engine/Vehicle, SUV/Pick-Up Engine/Vehicle, and Heavy-Duty Line Haul Engine) are being conducted in parallel with similar objectives and project activities. In the coming year, these projects will finish baseline tests with 8- and 15-ppm sulfur fuels and a low sulfur refinery fuel (called BP15) to characterize engine-out emissions (no catalysts) during transient and steady-state operation. Aging tests on complete catalyst systems will be initiated with emissions tests conducted every 50 hours up to 300 hours using 8- and 15-ppm S fuels and BP15 over the FTP, US06, and HFET cycles for the passenger car and SUV/Pick-Up projects and the HD FTP and 13-mode steady-state tests for the heavy-duty project. This will be followed by extended catalyst system aging and testing every 100 hours for up to 1500 hours depending on the project. A limited amount of testing will also be conducted with 30-ppm S fuel to determine the impact of misfueling with a higher sulfur fuel. Study of fuel properties other than sulfur to determine their impact on the NO_x adsorber/DPF systems will then be initiated and assessed more thoroughly during the second phase of the APBF-DEC activity.

- Field testing of ECD-1: Additional results, including polycyclic aromatic hydrocarbons (PAH), nitro-PAH (n-PAH), and 1,3-butadiene, from the chemical characterization will be published in FY03.
- Lube Oil Contribution to PM: Southwest Research Institute will measure the contribution of synthetic and mineral-based lubricating oil to PM emissions in combination with advanced fuels relative to a base fuel representative of those expected in 2007.
- Sandia National Laboratories: SNL will measure test-fuel lift-off lengths in their optical engine and compare to results from the Diesel Combustion Simulation Facility (DCSF). They will also study multiple-jet and jet-wall interactions and measure test-fuel soot distributions using a quantitative laser-extinction diagnostic. They will continue accelerator mass spectrometry experiments with oxygenates and expand the scope to include other fuel constituent molecules. Development of in-cylinder NO_x measurement capabilities to study combined effects of fuels and operating conditions on NO_x evolution will be initiated.
- Effect of Oxidation Catalysts on PM: CRC will conduct emissions tests on catalyst 3 (the one with the highest metal loading), and chemical analyses will be completed on the exhaust samples. A final report will be prepared.
- Emissions Tests of Advanced Diesel Fuels: Southwest Research Institute will test six advanced fuels (oxygenated and water emulsion fuels) in a vehicle with a state-of-the-art CIDI engine. The baseline fuel will be representative of diesel fuel properties expected in 2007. The vehicle will be equipped with advanced emission control devices such as NO_x adsorbers and diesel particulate filters.
- PM Emission Toxicology: Southwest Research Institute will investigate of the role of fuels in reducing tailpipe exhaust emissions of potentially toxicologically relevant compounds, from an advanced CIDI engine using a diesel oxidation catalyst and a catalyzed particulate filter.
- Impact of Oxygenates on PM and NO_x Formation: LLNL will extend its model capabilities to include additional oxygenated blending compounds and increase collaborations with projects outside LLNL dealing with diesel fuel issues.
- Systems Emission Reduction (SER) Analysis: NREL will analyze pathways for reducing emissions from the three vehicle platforms and investigate specific applications of analysis tools such as the effect of compression ratio, EGR, and aftertreatment devices on efficiency, and fuel formulation effects on emissions. A process to validate the model at a systems level will be developed, and relevant data from research partners will be identified and collected.

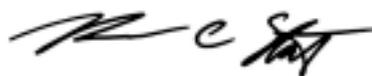
- Fuels Property Database: NREL will continue to populate fuels and emissions databases with light-duty engine and vehicle emissions data. The APBF-DEC projects will be a prime source of data, along with other DOE-sponsored research projects.
- Tracing of Fuel Components in PM Emissions Using Accelerator Mass Spectrometry: LLNL will determine the contributions of major fuel components to soot production, including selected oxygenates. They will also apply tracing techniques to measure the contribution of aromatics and cyclo-alkanes to emission products in diesel engines. Carbon-14 labeled lube oil will be obtained to determine the contribution of lube oil to soot and CO₂ emissions.

SUMMARY

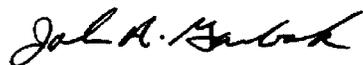
Advanced petroleum-based fuels enable the use of high efficiency prime movers such as CIDI engines to create clean and fuel efficient light-duty and heavy-duty vehicles with the attributes that consumers demand. Fuel efficient vehicles with very low emissions are essential to meet the challenges of climate change, energy security, and improved air quality. The work being conducted on advanced petroleum-based fuels complements the efforts to build advanced engines and fuel cells while recognizing that the engine, fuel, and emission control system must work together to achieve the maximum benefits possible. As the new fiscal year begins, we look forward to on-going and new cooperative efforts with the auto and energy industries to develop new and innovative technologies that will be used to make advanced transportation vehicles that are fuel-efficient, clean, and safe.



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II. FUEL/LUBRICANT EFFECTS TESTING ON ENGINE PERFORMANCE

A. Oil Consumption Contribution to CIDI PM Emissions during Transient Operation

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This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

A. Fuel Property Effects on Engine Emissions and Efficiency

Tasks

2. Fuel & Lubricant Properties - Engine-Out Emissions

Objective

- Quantify the effect of crankcase lubricant type on exhaust emissions measured during transient tests of a light-duty vehicle powered by a state-of-the-art CIDI engine.

Approach

- A European Mercedes C 220 D vehicle (OM611 engine) will be tested for transient exhaust emissions following the chassis dynamometer portion of the light-duty Federal Test Procedure (FTP-75) and US06 test cycles. Synthetic and mineral-based crankcase lubricants will be tested in combination with advanced fuels to determine the effect of lubricant composition on PM and other exhaust emissions.

Accomplishments

- Testing was delayed pending the availability of a special base fuel that is a refinery produced prototype of 2007 U.S. ultra-low-sulfur diesel fuel. The test lubricants have all been obtained and conditioned in an OM611 test engine to reduce volatile light ends. Testing is currently in progress.

Introduction

The Phase 1 project, "Impact of Consumed Lube Oil on Advanced CIDI Engine Emissions," revealed a significant impact of consumed oil on particulate matter (PM) under low-power steady-state conditions and an insignificant impact over the high-power, FTP

heavy-duty, transient test cycle. However, the impact of consumed oil was not investigated for any light-duty transient test cycle.

In the previous project, it was determined by the direct filter injection gas chromatography (DFI/GC) technique that the oil-volatile organic fraction (VOF)

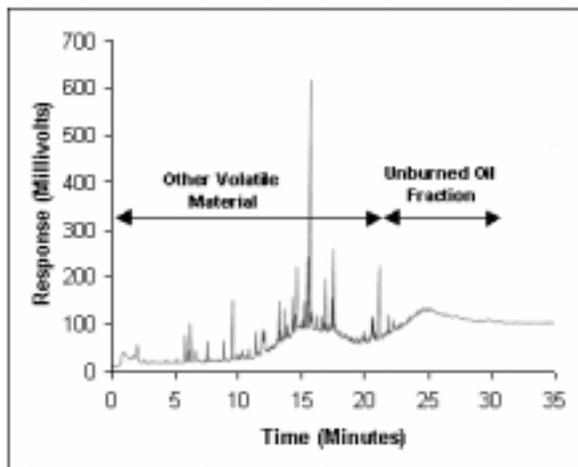


Figure 1. Gas Chromatogram of the VOF of PM

fraction can be reduced from 27% for a petroleum-based SAE 5W30 oil to 8% for a synthetic-based SAE 15W50. This illustrated that a PM reduction of approximately 19% is obtainable by changing the lubricant. This reduction was observed under steady-state, light-duty conditions when using California Air Resources Board (CARB) fuel. The fundamental question is whether the impact of consumed oil on PM emissions over the light-duty transient cycle will be similar to the impact observed over the low-power steady-state conditions investigated as part of the Phase 1 study.

Approach

A European Mercedes-Benz C220D vehicle will be tested for transient exhaust emissions following the light-duty FTP-75 and US06 test cycles. Synthetic and mineral-based lubricants will be tested in combination with advanced fuels to determine the effect of lubricant composition on PM.

The European Mercedes-Benz C220D is equipped with the OM611 engine. This advanced four-valve-per-cylinder CIDI engine is turbocharged and intercooled, and it includes a high-pressure common rail fuel injection system with pilot injection, exhaust gas recirculation, and intake port cut-off. The vehicle is equipped with a close-coupled oxidation catalyst and "lean NO_x" catalyst technology.

All evaluations will be conducted in triplicate over the chassis dynamometer portion of the FTP-75 and the US06 driving cycles.

An ultra-low-sulfur baseline fuel (BP15), formulated to be representative of expected U.S. diesel fuel in 2007, will be used for the initial evaluation of lubricant contribution to PM. The following lubricants will be included in the test matrix: synthetic SAE 5W30, mineral SAE 5W30, synthetic SAE 15W50, and synthetic SAE 0W30. In addition, FTP 75 and US06 tests will be conducted using the same lubricants and a fuel blend of BP15 Fuel with an advanced oxygenate (tripropylene glycol monomethyl ether-TPGME) blended to provide 7% oxygen in the fuel.

Exhaust constituents will be analyzed as specified below:

Constituent	Analysis Method
Total Hydrocarbon	Heated Flame Ionization Detector
Carbon Monoxide	Non-Dispersive Infrared Analysis
Carbon Dioxide	Non-Dispersive Infrared Analysis
Oxides of Nitrogen	Chemiluminescent Analysis
Particulate Matter	Gravimetric
Volatile Organic Fraction of PM	Direct Filter Injection Gas Chromatography
Oil Fraction of VOF	Direct Filter Injection Gas Chromatography

Figure 1 shows a gas chromatogram of the volatile organic fraction (VOF) of PM. The VOF is fractionated into unburned oil and other volatile material.

Appropriate statistical techniques will be used to determine differences between the PM and other exhaust emissions for each lubricant and each lubricant/fuel combination.

Results

The project was delayed pending the availability of the BP15 Fuel. Testing is under way, and some preliminary results are discussed as follows.

Triplicate FTP and US06 tests have been completed for the mineral SAE 5W30, the synthetic SAE 15W50 using BP15 fuel, and the blend of BP15 fuel with TPGME. Initial FTP results show a 2.5% fuel economy penalty for the SAE 15W50 oil as compared to the mineral (baseline) SAE 5W30 oil when using BP15 fuel.

The oxygenated fuel blend had a fuel economy penalty of approximately 2-3 miles per gallon for most test cycles. Over the FTP cycle, the oxygenated fuel reduced particulate matter by approximately 53%, compared to neat BP15 fuel. This effect was observed for both oils tested to date. FTP NO_x emissions with the oxygenated fuel were increased by 16 to 25%. Additional tests are continuing.

Conclusions

The project will be completed early in 2003.

III. FUEL & LUBRICANT EFFECTS ON EMISSION CONTROL SYSTEM PERFORMANCE

A. Durability of NO_x Adsorbers Using Ultra-Low Sulfur Fuels (Passenger Car Project)

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Other Participants: American Petroleum Institute (API), Engine Manufacturers Association (EMA), Manufacturers of Emissions Control Association (MECA), U. S. Environmental Protection Agency (EPA), Oak Ridge National Laboratory (ORNL), California Air Resources Board (CARB)

Subcontractor: FEV Engine Technology, Auburn Hills, MI

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

- B. Fuel Property Effects on Exhaust Emission Control System Technology
- C. Emission Control System Degradation
- D. Sulfur Impacts

Tasks

- 3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Determine the influence of diesel fuel composition on the ability of NO_x adsorber technology, in conjunction with diesel particulate filters (DPFs), to achieve stringent emissions levels with minimal fuel economy impact.
- Achieve Tier 2 Bin 5 emission standards of 0.07 g/mi NO_x and 0.01 g/mi PM.
- Determine the necessary fuel sulfur level and other fuel properties that will enable high performance of these NO_x adsorber/DPF systems.

Approach

A model year 2001 Audi A4 Avant with a 1.9 liter TDI engine (100 KW at 4000 rpm) with a Bosch common rail second generation fuel injection system, integrated exhaust gas recirculation (EGR) and a Garrett GT 17 V turbine will be used as the test vehicle for this project. This vehicle will be equipped with appropriately designed emission control devices and the necessary regenerative control hardware and electronics to meet the project objectives. This project includes three major tasks:

- Task A involves development of the test platform including setup, integration, and optimization of the engine, rapid warm-up testing and thermal management; emission control system (ECS), and associated electronic controls; and baseline (engine-out) testing of regulated and unregulated (toxic) emissions.
- Task B involves system performance and aging tests using fuels with varying sulfur content (8-, 15-, 30-ppm S) and periodic evaluations of emissions over the FTP, US06, and HFET during aging tests up to 1000 hours of operation. Two single-leg ECS architectures will be developed and tested.
- Task C will investigate fuel properties other than sulfur and determine their impact on the NO_x adsorber/DPF system. This testing will include an ultra-low sulfur (<15-ppm S) refinery fuel and up to three additional fuels. No aging tests will be conducted in Task C.

Accomplishments

- Acquired test vehicle and four engines and installed one engine in vehicle and two engines in emissions test cells
- Designed ECS architecture and completed exhaust system modifications
- Integrated an external electronic controller with the base engine electronics to control post injection and lean and rich cycling conditions necessary for catalyst regeneration
- Developed rapid warm-up procedures and other thermal management approaches
- Developed protocols for sampling and analysis of unregulated toxic emissions
- Completed initial ECS system regeneration and desulfurization strategies

Future Directions

- Complete the development of catalyst regeneration and desulfurization strategies (Task A)
- Conduct durability testing with fuels of varying sulfur content (Task B)
- Conduct testing of other fuel properties (Task C)

Introduction

The Advanced Petroleum Based Fuels – Diesel Emission Control (APBF-DEC) activity is a joint government/industry research effort to determine the best combinations of low-sulfur diesel fuels, lubricants, diesel engines, and emission control systems to meet projected emission standards for the 2002 to 2010 time period. The project leverages the participation of several multi-industry working groups that direct five individual projects.

This project aims to demonstrate the viability of combining NO_x adsorber catalysts and DPF technologies in combination with clean fuels, advanced engines and electronic controls to achieve stringent emission levels while maintaining high fuel economy. Specifically, this project will identify the fuels needed to enable these technologies for use in light-duty vehicles. The goal for this platform is to meet stringent Tier 2 Bin 5 light-duty emission standards with limits of 0.07 g/mi NO_x and 0.01 g/mi PM.



Figure 1. Audi A4 Avant Test Vehicle

Another critical focus of this project is the characterization of currently unregulated, but potentially toxic emissions.

Among the fuel variables to be studied, sulfur has been identified as most critical to this research. The Diesel Emission Control – Sulfur Effects (DECSE) project [1], a predecessor to this effort, examined the effect of sulfur on individual emission control devices including NO_x adsorber catalysts, DPFs, diesel oxidation catalysts (DOC), and lean- NO_x catalysts. This testing showed that efficiency of NO_x adsorber catalysts is significantly effected by sulfur in the diesel fuel [2]. This project provides a more thorough investigation of sulfur effects and uses modern hardware and robust electronic controls with systems incorporating both NO_x and PM control devices. Emission control system durability, as a function of fuel sulfur content, will be examined in tests up to 1000 hours in duration.

Approach

The 2001 Audi A4 Avant test vehicle (Figure 1) with a 1.9 liter TDI engine (100 KW at 4000 rpm) (Figure 2) will be equipped with appropriately designed emission control devices and the necessary regenerative control hardware and electronics to conduct this fuel study. As illustrated in Figure 3, a significant reduction in tail pipe emissions over the current European calibration for this vehicle will be required for this project.

In order to make the goals of this project possible and limit the reduction efficiencies required by the



Figure 2. 1.9L TDI Test Engine

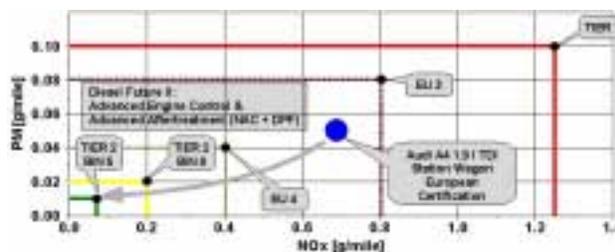


Figure 3. Project Emission Reduction Targets

aftertreatment devices significant modifications have been made to the test engine to lower engine-out emissions, including: installation of common rail fuel injectors, addition of an aluminum cylinder head, and engine calibration changes (for lower engine-out NO_x and more favorable exhaust temperature profiles). In addition, dual wall insulated exhaust components will be used to retain heat for the ECS. MECA has provided emission control devices for two different ECS configurations, both single leg systems. Figure 4 shows the basic configuration for both systems, with the key difference being the formulation of the pre-catalyst. In one system the pre-catalyst will serve both a NO_x adsorbing and oxidizing function, while in the second system the pre-catalyst will only serve a NO_x adsorbing function. This project is comprised of three major tasks as described in the following.

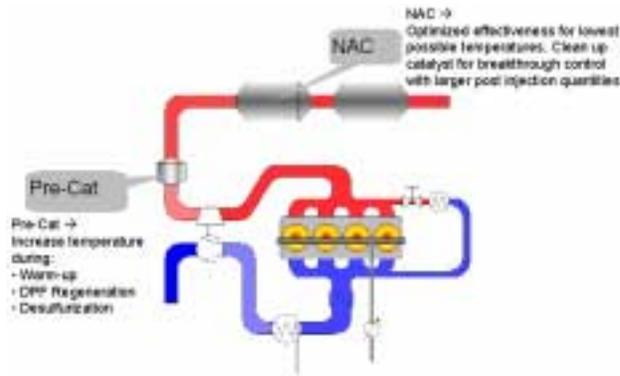


Figure 4. Emission Control System Architecture

Task A involves development of the test platform including setup, integration, and optimization of the engine and vehicle, emission control system (ECS), associated electronic controls and development of thermal management strategies. This task includes the design of post injection strategies that will provide in-cylinder secondary fuel for NO_x adsorber catalyst regeneration. This task also includes baseline tests to characterize engine-out emissions (no catalysts) during transient and steady-state operation. Baseline tests will be conducted with 8- and 15-ppm sulfur fuels and a low sulfur refinery fuel (called BP15).

Task B involves system performance and aging evaluations using fuels with varying fuel sulfur content. Performance evaluations on the FTP, US06 and HFET will be conducted every 50 hours up to 300 hours using 8- and 15-ppm S fuels. Both ECSs will be tested with each fuel. Aging will continue on one of these systems for an additional 1000 hours using the 15-ppm S fuel to determine longer term aging impacts. A limited amount of testing will also be conducted with 30-ppm S fuel to determine the impact of misfueling with a higher sulfur fuel.

Task C is a study of fuel properties other than sulfur to determine their impact on the NO_x adsorber/DPF system. This testing will include an ultra-low sulfur (<15-ppm S) refinery fuel and up to three additional fuels. Each fuel will be tested to determine its effect on the regeneration and desulfurization strategies developed in Task A. No aging tests will be conducted in Task C.

A full suite of emissions will be measured during Task A baseline testing and Task B aging tests. They include the following:

- NO_x
- CO
- HC (hydrocarbons)
- CO₂ (carbon dioxide)
- PM (including detailed compositional analysis)
- Benzene
- 1,3 butadiene
- Formaldehyde
- Acetaldehyde
- N₂O (nitrous oxide)
- NH₃ (ammonia)
- SO₂ (sulfur dioxide)
- H₂S (hydrogen sulfide)
- Nitroxyalkanes

Results

A majority of the effort to date has been devoted to procurement and setup of the testing platforms as well as development of strategies for regeneration and desulfurization. A limited amount of baseline and engine-out data has been collected. Aging and evaluations testing will generate a significant body of data in FY 2003.

References

1. <http://www.ott.doe.gov/decse/>
2. U.S. Department of Energy, Engine Manufacturers Association, Manufacturers of Emission Controls Association, "Diesel Emission Control – Sulfur Effects (DECSE) Program – Phase I Interim Data Report No. 2: NO_x Adsorber Catalysts," October 1999.

B. Durability of NO_x Adsorbers Using Ultra-Low Sulfur Fuels (Pick-up/SUV Project)

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Other Participants: American Petroleum Institute (API), Engine Manufacturers Association (EMA), Manufacturers of Emissions Control Association (MECA), U. S. Environmental Protection Agency (EPA), Oak Ridge National Laboratory (ORNL), California Air Resources Board (CARB)

Subcontractor: Southwest Research Institute, San Antonio, TX

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

B. Fuel Property Effects on Exhaust Emission Control System Technology

C. Emission Control System Degradation

D. Sulfur Impacts

Tasks

3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Demonstrate the potential of NO_x adsorber technology in combination with diesel particulate filters, advanced fuels, and advanced engine controls to achieve stringent emission levels while maintaining high fuel economy. Achieve stringent Tier 2 Bin 5 light-duty emission standards with limits of 0.07 g/mi NO_x and 0.01 g/mi particulate matter (PM).
- Determine the necessary fuel sulfur level and other fuel properties that will enable these systems. The fuel sulfur levels tested will be representative of those required to be available beginning June 2006 (<15 ppm S).

Approach

A model year 2002 Chevrolet 2500 Series Silverado with a 6.6 liter Duramax engine (300 HP at 3100 rpm) with a Bosch common rail fuel injection system, integrated exhaust gas recirculation (EGR), charge air cooler, and a center mounted turbine will be used as the test vehicle for this project. This vehicle will be equipped with appropriately designed emission control devices and the necessary regenerative control hardware and electronics to meet the project objectives. This project includes three major tasks:

- Task A involves development of the test platform including setup, integration, and optimization of the engine; thermal management; emission control system (ECS) and associated electronic controls; and baseline (engine-out) testing of regulated and unregulated emissions.
- Task B involves system performance and aging tests using fuels with varying sulfur content (8, 15, 30 ppm S) and periodic evaluations of emissions over the FTP, US06, and HFET driving cycles during aging tests up to 1500 hours duration. Two ECS architectures will be developed and tested: a single leg system (System A) and a dual leg system (System B).
- Task C will investigate fuel properties other than sulfur and determine their impact on the NO_x adsorber/diesel particulate filter (DPF) system. This testing will include an ultra-low sulfur (<15 ppm S) refinery fuel and up to two additional fuels. No aging tests will be conducted in Task C.

Accomplishments

- Acquired test vehicles and engines, and installed two engines in emissions test cells.
- Designed ECS architecture and completed exhaust system modifications.
- Integrated an external electronic controller with the base engine electronics to control post injection and lean and rich cycling conditions necessary for catalyst regeneration.
- Developed and tested rapid warm-up procedures and other thermal management approaches.
- Developed protocols for sampling and analysis of unregulated toxic emissions.
- Completed initial ECS system regeneration and desulfurization strategies.

Future Directions

- Complete the development of catalyst regeneration and desulfurization strategies (Task A).
- Conduct durability testing with fuels of varying sulfur content (Task B).
- Conduct testing of other fuel properties (Task C).

Introduction

The Advanced Petroleum Based Fuels - Diesel Emission Control (APBF-DEC) activity is a joint government/industry research effort to determine the best combinations of low-sulfur diesel fuels, lubricants, diesel engines, and emission control systems to meet projected emission standards for the 2002 to 2010 time period. The project leverages the participation of several multi-industry working groups that direct five individual projects.

This project aims to demonstrate the viability of combining NO_x adsorber catalysts and DPF technologies in combination with clean fuels, advanced engines and electronic controls to achieve stringent emission levels while maintaining high fuel economy. Specifically, this project will identify the fuels needed to enable these technologies for use in light-duty vehicles. The goal for this platform is to meet stringent Tier 2 Bin 5 light-duty emission

standards with limits of 0.07 g/mi NO_x and 0.01 g/mi PM. Another critical focus of this project is the characterization of currently unregulated, but potentially toxic emissions.

Among the fuel variables to be studied, sulfur has been identified as most critical to this research. The Diesel Emission Control - Sulfur Effects (DECSE) project [1], a predecessor to this effort, examined the effect of sulfur on individual emission control devices including NO_x adsorber catalysts, DPFs, diesel oxidation catalysts (DOC), and lean-NO_x catalysts. This testing showed that efficiency of NO_x adsorber catalysts is significantly affected by sulfur in the diesel fuel [2]. This project provides a more thorough investigation of sulfur effects and uses modern hardware and robust electronic controls with systems incorporating both NO_x and PM control devices. Emission control system durability, as a function of fuel sulfur content, will be examined in tests up to 1500 hours in duration.

Approach

A model year 2002 Chevrolet 2500 Series Silverado (Figure 1) with a 6.6 liter Duramax engine (300 HP at 3100 rpm) (Figure 2) will be equipped with appropriately designed emission control devices and the necessary regenerative control hardware and electronics to meet project objectives. A significant reduction in tailpipe emissions over the current California calibration for this vehicle will be required to meet the emissions objectives of this project.

In order to make the objectives of this project possible and limit the reduction efficiencies required by the aftertreatment devices, significant modifications have been made to the test engine to lower engine-out emissions. These include installation of low pressure EGR, a turbo by-pass system, and engine calibration changes (for lower engine-out NO_x and more favorable exhaust temperature profiles). In addition, secondary injection and dual wall insulated exhaust components

will be used to retain heat for the ECS. MECA has provided emission control devices for two different ECS configurations: a single leg system (System A) and a dual leg system (System B). Figures 3 and 4 show the basic configuration for both systems. System A is a simple configuration which will minimize the packaging difficulties and catalyst costs, while System B will minimize NO_x breakthrough as well as fuel consumption penalties associated with regeneration, but will be more complex and expensive. This project includes three major tasks:

Task A involves development of the test platform including setup, integration, and optimization of the engine and vehicle, emission control system (ECS), associated electronic controls, and development of thermal management strategies. This task includes the design of post injection strategies that will provide in-cylinder secondary fuel for NO_x adsorber catalyst regeneration. This task also includes



Figure 1. 2002 Chevrolet 2500 Series Silverado



Figure 2. 6.6 Liter Duramax Engine

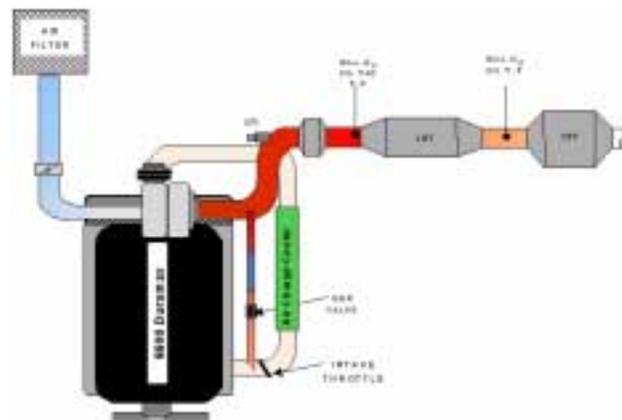


Figure 3. Single-leg ECS Configuration (System A)

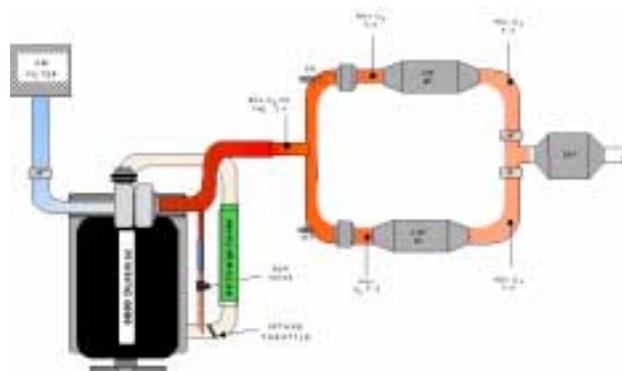


Figure 4. Double-leg ECS Configuration (System B)

baseline tests to characterize engine-out emissions (no catalysts) during transient and steady-state operation. Baseline tests will be conducted with 8 and 15 ppm sulfur fuels and a low sulfur refinery fuel (called BP15).

Task B involves system performance and aging evaluations using fuels with varying fuel sulfur content. Performance evaluations on the FTP, US06 and HFET driving cycles will be conducted every 50 hours up to 300 hours using 8 and 15 ppm sulfur fuels. Both ECSs will be tested with each fuel. Aging will continue on one of these systems for an additional 1500 hours using the 15 ppm sulfur fuel to determine longer term aging impacts. A limited amount of testing will also be conducted with 30 ppm sulfur fuel to determine the impact of misfueling with a higher sulfur fuel.

Task C is a study of fuel properties other than sulfur content to determine their impact on the NO_x adsorber/DPF system. This testing will include an ultra-low sulfur (<15 ppm sulfur) refinery fuel and up to two additional fuels. Each fuel will be tested to determine its effect on the regeneration and desulfurization strategies developed in Task A. No aging tests will be conducted in Task C.

A full suite of emissions will be measured during Task A baseline testing, Task B aging tests, and Task C. They include the following:

- NO_x
- CO
- HC (hydrocarbons)
- CO₂ (carbon dioxide)
- PM (including detailed compositional analysis)
- Benzene
- 1,3 butadiene
- Formaldehyde
- Acetaldehyde
- N₂O (nitrous oxide)
- NH₃ (ammonia)
- SO₂ (sulfur dioxide)
- H₂S (hydrogen sulfide)
- Nitroxyalkanes

Results

A majority of the effort to date has been devoted to procurement and setup of the testing platforms as well as development of strategies for regeneration and desulfurization. A limited amount of baseline and engine-out data has been collected. Aging and evaluations testing will generate a significant body of data in FY 2003.

References

1. <http://www.ott.doe.gov/decse/>
2. U.S. Department of Energy, Engine Manufacturers Association, Manufacturers of Emission Controls Association, "Diesel Emission Control - Sulfur Effects (DECSE) Program - Phase I Interim Data Report No. 2: NO_x Adsorber Catalysts," October 1999

C. Durability of NO_x Adsorbers Using Ultra-Low Sulfur Fuels (Heavy-Duty Project)

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Other Participants: American Chemistry Council, American Petroleum Institute (API), Engine Manufacturers Association (EMA), Manufacturers of Emissions Control Association (MECA), U. S. Environmental Protection Agency (EPA), Oak Ridge National Laboratory (ORNL), California Air Resources Board (CARB), South Coast Air Quality Management District (SCAQMD)

Main Subcontractor: Ricardo, Inc., Burr Ridge, Illinois

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

- B. Fuel Property Effects of Exhaust Emission Control System Technology
- C. Emission Control System Degradation
- D. Sulfur Impacts

Tasks

- 3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Demonstrate the viability of achieving future emissions standards for heavy-duty engines using nitrogen oxides (NO_x) adsorber catalyst and diesel particle filter (DPF) technologies without significantly compromising fuel economy.
- Determine the necessary fuel sulfur level and other fuel properties that will enable these systems. The fuel sulfur levels tested will be representative of those required to be available beginning June 2006 (<15 parts per million [ppm] sulfur [S]).

Approach

- A Cummins ISX engine (15L, 475 horsepower [hp]) with integrated exhaust gas recirculation (EGR) and variable geometry turbine (VGT) has been supplied to the project. This engine will be equipped with appropriately designed emission control devices and the necessary regenerative control hardware and electronics to conduct this fuel study, which encompasses three major tasks:
 - Task A involves development of the test platform including setup, integration, and optimization of the engine, emission control system (ECS), and associated electronic controls; modeling to determine appropriate regeneration and desulfurization strategies; and baseline (engine-out) testing of regulated and unregulated (toxic) emissions.

- Task B involves system performance and aging tests using fuels with varying sulfur content (8, 15, 30 ppm S) and periodic evaluations (transient and steady-state) of emissions during aging tests up to 1500 hours of operation. Two ECS architectures will be developed and tested: a single leg system and a twin-bed (dual NO_x adsorber catalysts) system.
- Task C will investigate fuel properties other than sulfur and determine their impact on the NO_x adsorber/DPF system. This testing will include an ultra-low sulfur (<15 ppm S) refinery fuel and up to three additional fuels. No aging tests will be conducted in Task C.

Accomplishments

- Installed ISX engine in emissions test cell.
- Designed and installed in-cylinder secondary injection system.
- Integrated an external electronic controller with the base engine electronics to control lean and rich exhaust conditions necessary for catalyst regeneration.
- Developed operational model of twin-bed NO_x adsorber/DPF system.
- Developed protocols for sampling and analysis of unregulated toxic emissions.
- Completed baseline engine-out emissions tests.

Future Directions

- Complete the development of catalyst regeneration and desulfurization strategies (Task A).
- Conduct durability testing with fuels of varying sulfur content (Task B).
- Conduct testing of other fuel properties (Task C).

Introduction

The Advanced Petroleum Based Fuels - Diesel Emission Control (APBF-DEC) activity is a joint government/industry research effort to determine the best combinations of low-sulfur diesel fuels, lubricants, diesel engines, and emission control systems to meet projected emission standards for the 2002 to 2010 time period. The project leverages the participation of several multi-industry working groups that direct five individual projects.

This project aims to demonstrate the viability of combining NO_x adsorber catalysts and DPF technologies in combination with clean fuels, advanced engines and electronic controls to achieve stringent emission levels while maintaining high fuel economy. Specifically, this project will identify the fuels needed to enable these technologies for use in heavy-duty on-highway engines. For these engines, a NO_x standard of 0.2 g/bhp-hr and 0.01 g/bhp-hr ppm will be phased in between 2007 and 2010. These emission levels must be achievable not only

over the transient HD Federal Test Procedure, but also in other modes of operation. Another critical focus of this project is the characterization of currently unregulated, but potentially toxic emissions.

Among the fuel variables to be studied, sulfur has been identified as most critical to this research. The Diesel Emission Control - Sulfur Effects (DECSE) project [1], a predecessor to this effort, examined the effect of sulfur on individual emission control devices including NO_x adsorber catalysts, DPFs, diesel oxidation catalysts (DOC), and lean-NO_x catalysts. This testing showed that efficiency of NO_x adsorber catalysts is significantly affected by sulfur in the diesel fuel [2]. This project provides a more thorough investigation of sulfur effects and uses modern hardware and robust electronic controls with systems incorporating both NO_x and PM control devices. Emission control system durability, as a function of fuel sulfur content, will be examined in tests up to 1500 hours in duration.



Figure 1. Installation of Secondary In-Cylinder Fuel Injectors

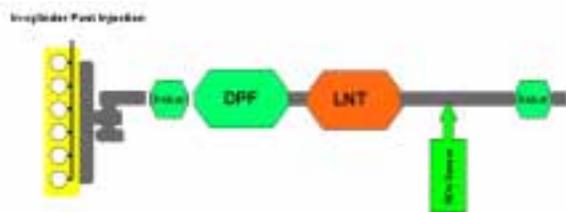


Figure 2. Emission Control System 'A': Single Leg Architecture

Approach

The engine selected for this study is a Cummins ISX, a 15L, 500 hp inline, 6-cylinder engine with dual overhead camshafts. It is equipped with integrated EGR and a VGT and is calibrated to meet the 2004 HD emission standards (2.5 g/bhp hr NO_x, 0.1 g/bhp hr PM) as received. Additional modifications have been made by the subcontractor, including: installation of secondary in-cylinder fuel injectors (Figure 1), and engine calibration changes (for lower engine-out NO_x and more favorable exhaust temperature profiles). MECA has provided emission control devices for two different ECS configurations: a single leg system (System A, Figure 2), and a twin-bed architecture (System B, Figure 3). The project involves three major tasks.

Task A involves development of the test platform, including setup, integration, and optimization of the engine, emission control system

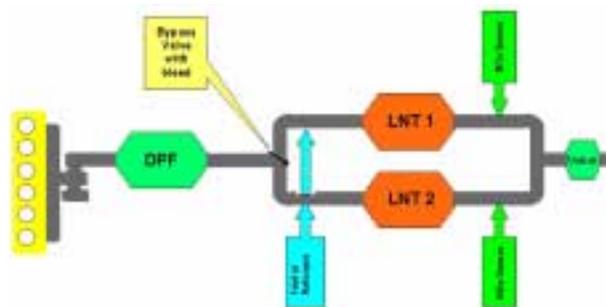


Figure 3. Emission Control System 'B': Twin Bed Architecture

(ECS), and associated electronic controls. This task includes the design and installation of supplemental injectors that will provide in-cylinder secondary fuel for NO_x adsorber catalyst regeneration. Modeling is being conducted to determine the appropriate regeneration and desulfurization conditions for optimal performance and system durability. This task also includes baseline tests to characterize engine-out emissions (no catalysts) during transient and steady-state operation. Baseline tests will be conducted with 8 and 15 ppm sulfur fuels and a low sulfur refinery fuel (called BP15).

Task B involves system performance and aging evaluations using fuels with varying fuel sulfur content. Performance evaluations, including the HD Federal Test Procedure and 13-mode steady-state tests, will be conducted every 50 hours up to 300 hours using 8 and 15 ppm S fuels. Both systems (A and B) will be tested with each fuel. Aging will continue on one of these systems for an additional 1000-1200 hours using the 15 ppm S fuel to determine longer term aging impacts. A limited amount of testing will also be conducted with 30 ppm S fuel to determine the impact of misfueling with a higher sulfur fuel.

Task C is a study of fuel properties other than sulfur to determine their impact on the NO_x adsorber/DPF system. This testing will include an ultra-low sulfur (<15 ppm S) refinery fuel and up to three additional fuels. Each fuel will be tested to determine its effect on the regeneration and desulfurization strategies developed in Task A. No aging tests will be conducted in Task C.

A full suite of emissions will be measured during Task A baseline testing, Task B aging tests, and Task C. They include the following:

- NO_x
- CO
- HC (hydrocarbons)
- CO₂ (carbon dioxide)
- PM (including detailed compositional analysis)
- Benzene
- 1,3 butadiene
- Formaldehyde
- Acetaldehyde
- N₂O (nitrous oxide)
- NH₃ (ammonia)
- SO₂ (sulfur dioxide)
- H₂S (hydrogen sulfide)

Results

A majority of the effort to date has been devoted to procurement and setup of the testing platforms as well as development of strategies for regeneration and desulfurization. A limited amount of baseline (engine-out) data has been collected. Aging and evaluations testing will generate a significant body of data in FY 2003.

References

1. <http://www.ott.doe.gov/decse/>
2. U.S. Department of Energy, Engine Manufacturers Association, Manufacturers of Emission Controls Association, "Diesel Emission Control - Sulfur Effects (DECSE) Program - Phase I Interim Data Report No. 2: NO_x Adsorber Catalysts," October 1999

D. Lubricant Property Impact on CIDI Emission Control System Durability

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Other Participants: American Chemistry Council, American Petroleum Institute (API), Engine Manufacturers Association (EMA), Manufacturers of Emissions Control Association (MECA), Oak Ridge National Laboratory (ORNL)

Main Subcontractor: Automotive Testing Laboratories, Inc., East Liberty, Ohio

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

- B. Fuel Property Effects of Exhaust Emission Control System Technology
- C. Emission Control System Degradation
- D. Sulfur Impacts

Tasks

- 3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Determine the impact of lubricant properties and composition on engine-out/catalyst-in emissions.
- Determine if lubricant formulation impacts the performance and durability of diesel engine emission control systems (ECS).
- Develop guidelines for the specification of catalyst compatible lubricants required for use in future low-emissions diesel engines.

Approach

- Phase 1. Determine the impact of lubricant formulation (additives and basestock) on the emissions of a compressed ignition direct injection (CIDI) engine. Conventional and developmental additives blended with four different basestocks are tested in a medium-duty diesel engine.
- Phase 2. Develop a rapid catalyst aging protocol to accelerate studies to determine the impact of lubricant derived emissions on emission control system durability.
- Phase 3. Perform testing to study lubricant effects on NO_x adsorber catalysts and selective catalytic reduction in combination with diesel particle filters.

Accomplishments

- An International T444E (7.3L, V8) has been installed in an emissions test cell at ATL. The MY 1999 engine has been upfit with exhaust gas recirculation (EGR) and closed crankcase ventilation (CCV) hardware similar to future base engine designs.
- Test lubricants ranging in sulfur content between 0 and 6500 parts per million (ppm) and ash between 0% and 1.85% have been prepared in four basestocks; one each from the four major base oil classifications (Group I-IV) as defined by API.
- All Phase I testing, including 12 additives and four basestocks, has been completed.

Future Directions

- The influence of the lubricant derived emission components on catalyst durability will be examined.
- A rapid aging protocol to accelerate lubricant effects testing will be developed and utilized to determine if consumed diesel engine oil impacts catalyst life.

Introduction

The Diesel Emission Control - Sulfur Effects project [1] quantified the impact of diesel fuel sulfur on the performance and short-term durability of diesel emission control devices. The acute sensitivity of certain of these devices highlighted the need to study another source of sulfur and other potential poisons - specifically the diesel lubricating oil.

To address this concern, a research project to study lubricant formulation (basestocks and additives) effects on diesel emission control systems is entering its second year. The research is being conducted as part of the Department of Energy's Advanced Petroleum Based Fuels - Diesel Emission Control activity and leverages participation from an inter-industry working group that guides the research.

It is anticipated that the results of this study will be critical in defining the needs of future lubricant formulations for both light-duty and heavy-duty diesel engines. Should a need for substantial lubricant reformulations be identified, industry will require significant development time to research 'catalyst compatible' formulations that are cost-competitive and that continue to deliver superior engine protection and long life that engine customers demand. In addition, engine manufacturers recognize that the lubricant reformulations may drive the need for more robust engine hardware that is tolerant of modified oil chemistry, an endeavor requiring significant development time as well.



Figure 1. International T444E Engine Installation

Approach

This project is being conducted in three consecutive phases. The first phase, which identified and characterized lubricant derived emissions constituents, has been completed. This testing utilized a medium-duty International T444E engine that was equipped with EGR and CCV (Figure 1). A matrix of conventional and experimental lubricant additive packages blended with various petroleum-based and synthetic basestocks was evaluated. Twelve additive packages were selected to provide a range of various components including ash content, sulfur, zinc, phosphorus, etc. The four basestocks tested span the available production approaches and include products of varying sulfur content, volatility,

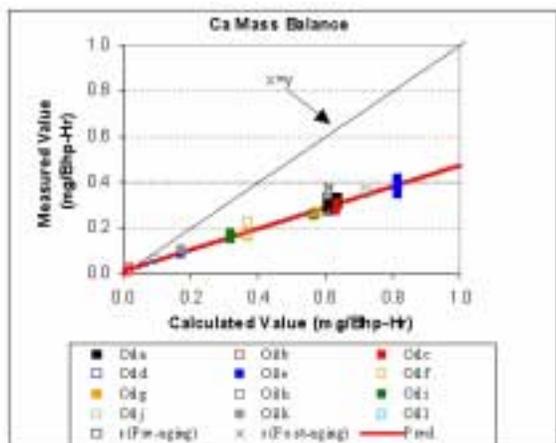


Figure 2. Calcium in PM Emissions

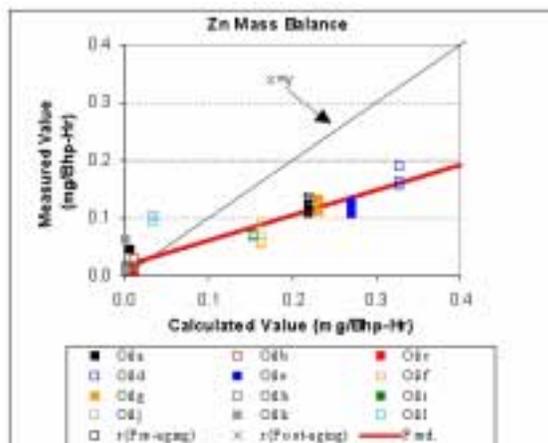


Figure 3. Zinc in PM Emissions

and degree of saturation. Emissions were sampled during a four mode steady-state operating cycle and included: gaseous hydrocarbons, carbon monoxide, sulfur dioxide, nitrogen oxides, and particulate matter (PM). The PM was further analyzed for sulfate and nitrate fractions, soluble organic fraction, metals content, and polycyclic aromatic hydrocarbon content.

Follow-up work is being conducted to determine if and to what extent these lubricant related emissions species impact the performance and durability of emissions control devices designed to reduce NO_x and PM emissions from diesel engines. A protocol for rapidly aging emission control devices and determining lubricant effects is being developed. This test protocol will then be utilized to determine if lubricant sulfur, ash, and certain metals need to be controlled to meet useful life standards placed on emission control systems.

Results

Mass balances were conducted for each of the critical parameters. Predicted emission rates for each species were estimated based upon fuel and lubricant properties and fuel and lubricant consumption rates. Data presented here compares predicted rates with the actual measured rates. As evidenced by Figure 2, calcium emission rates are directly correlated with the concentration of calcium in the oil, independent of any given additive formulation. However, only 46% of the calcium in the oil is emitted and

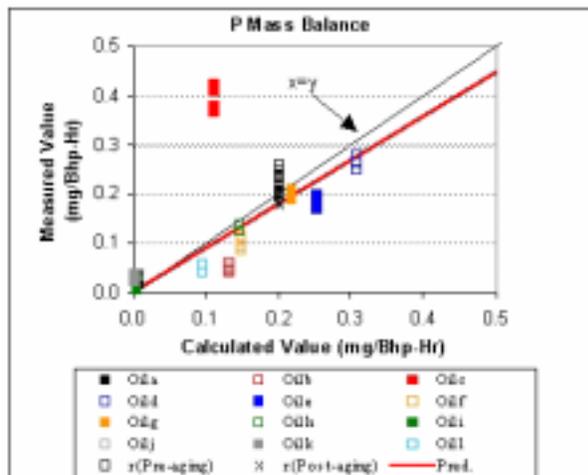


Figure 4. Phosphorus in PM emissions

measured in the PM. Several theories, including deposition in the lube oil filter, have been proposed. Clearly, though, the oil is not uniformly consumed.

Figure 3 illustrates the mass balance results for zinc. Like calcium, zinc emissions are directly correlated to the concentration in the tested formulation with 43% estimated recovery; however, one formulation showed a measurable deviation, suggesting that this oil is consumed by a mechanism dissimilar to the rest. Because most of the zinc is derived from the very surface active zinc dialkyl-dithiophosphate (ZDDP) antiwear agent, it is believed that a majority of the "missing" zinc has been deposited on metal surfaces.

Phosphorus emissions are shown in Figure 4. With the exception of one oil, the recovery of phosphorus is consistent with predictions (90%) and highly correlated with the phosphorus concentration of the oil. The emission rate from "Oil C" was nearly four times the predicted rate, suggesting that it is preferentially consumed in this formulation. This particular formulation contains a very low zinc concentration, suggesting that it utilizes non-traditional anti-wear chemistry (i.e. no ZDDP). As such, the phosphorus is more volatile and is emitted at a higher rate than predicted by the measured total oil consumption rate. This is a critical finding because it illustrates the danger in specifications utilizing chemical limits (e.g. controlling phosphorus levels in oils may not have the desired effect).

Because of the well documented impact of sulfur (in particular, SO_2) on the durability of NO_x adsorber catalysts [2], particular scrutiny has been given to the impact of lubricant derived sulfur on emissions of this catalyst poison. Figure 5 shows SO_2 emissions for the various additive and basestock combinations tested here. Additives A-F were tested in each of the four basestock groups while additives G-L (and the reference oil R) were tested exclusively in the Group II stock. Of the four basestocks tested, only the Group I stock had significant sulfur content (approx 5000-ppm S); the others were hydrotreated (II and III) or synthetic (IV, poly-alpha olefin). For reference, additive B contained almost no sulfur while additive E contributed 6590 ppm S in the additive system alone. In general, SO_2 emissions rates do not correlate well with the concentrations in the oil. Perhaps the most significant comparisons are between the B and E blends. While the total sulfur content with E is much greater than B, SO_2 emissions are quite similar within a given basestock. Basestocks do not have a significant effect either, although the synthetic (Group IV) basestock tends to give the lowest SO_2 emissions, independent of the additive system.

Conclusions

Sulfur content in the oil is generally related to sulfur emissions in the exhaust, but the type of sulfur compound in the oil can have a significant impact on the SO_2 emission rate. This is generally true for phosphorus emissions as well.

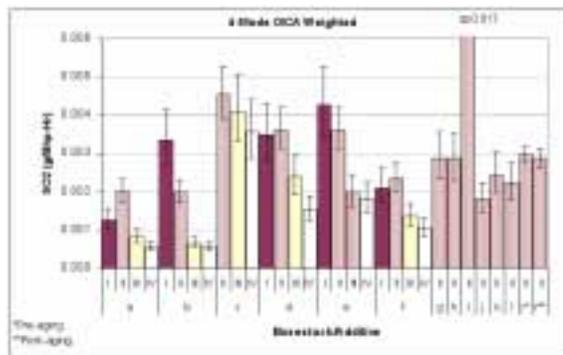


Figure 5. Base Oil and Additive Effects on SO_2 Emissions

Some compounds, such as zinc and calcium, may be found in the exhaust in lower quantities, on average, than predicted by the measured oil consumption.

References

1. <http://www.ott.doe.gov/decse/>
2. U.S. Department of Energy, Engine Manufacturers Association, Manufacturers of Emission Controls Association, "Diesel Emission Control - Sulfur Effects Program - Phase I Interim Data Report No. 2: NO_x Adsorber Catalysts," October 1999

E. Demonstration of Potential for Selective Catalytic Reduction and Diesel Particulate Filters

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Main Subcontractor: Southwest Research Institute (SwRI), San Antonio, Texas

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

B.Fuel Property Effects on Exhaust Emission Control System Technology

Tasks

3.Fuel & Lubricant Properties - Exhaust Emissions Control and Emissions

Objectives

- Demonstrate the low-emissions performance of advanced diesel engines operating on advanced fuels, and equipped with low-pressure-loop exhaust gas recirculation (EGR) plus urea selective catalytic reduction (SCR) and diesel particulate filters (DPF).
- Determine the regulated and unregulated emissions with and without emission controls.
- Examine the durability of the emission control systems.
- Determine toxic and unregulated emission levels.
- Evaluate the sensitivities of the emission controls to fuel variables.

Approach

- Set up a heavy-duty engine in an emissions test cell to optimize emission reduction performance of two different emission control systems utilizing urea SCR (System A and System B).
- Apply a low-pressure-loop EGR system to reduce engine-out nitrogen oxides (NO_x) to ~ 2.0 - 2.5 grams per horsepower per hour (g/hp-hr) or less.
- Add emission control system(s) including diesel particulate filters and SCR systems with urea injection to reduce tailpipe emissions of both NO_x and particulate matter (PM). (Two different emission control systems S Systems A and B S both comprised of DPF and SCR catalysts will be evaluated.)
- Integrate controls and optimize performance to reach the lowest possible emissions of NO_x and PM for both systems.
- Perform 6,000 hour durability tests simultaneously with Systems A and B, and measure emissions S regulated and unregulated S at 2,000 hour intervals.

Accomplishments

- A Caterpillar C-12 engine was installed in an emissions test cell and tested in its as-received configuration with D2 diesel fuel containing 350 ppm sulfur. Emissions results for the baseline over the U.S. heavy-duty transient cycle were ~ 3.55 g/hp-hr NO_x and ~ 0.065 g/hp-hr PM. Results over the steady-state European OICA cycle were 4.82 g/hp-hr NO_x and 0.031 g/hp-hr PM.
- The engine was fitted with a low-pressure-loop cooled EGR system, provided by STT-Emtech in Sweden and a diesel particulate filter (part of System A) provided by MECA, and the systems were optimized for low engine-out NO_x. Engine-out NO_x over the transient cycle with the EGR system and using Diesel Emission Control - Sulfur Effects (DECSE) program 3-ppm sulfur fuel was reduced to 1.5 g/hp-hr. Over the steady-state OICA cycle, NO_x emissions were reduced to 2.32 g/hp-hr. Particulate emissions for both tests remained below 0.01 g/bhp-hr.
- The urea SCR catalyst of System A was added to the emission control system along with urea injection systems provided by Robert Bosch, and the calibration of the SCR system for NO_x reductions was engineered. Results on the steady-state OICA test showed tailpipe NO_x reduced to only 0.17 g/hp-hr. The calibration is being optimized at this time for the transient cycle.
- A test cell has been set up at Southwest Research Institute (SwRI) for the durability tests using two C12 engines provided by Caterpillar.

Future Directions

- Calibration of System A for low emissions will be completed soon. Then, a matrix of emission tests with the different fuels will be carried out before the system is installed on one of the durability engines for the beginning of the 6,000-hour durability test.

Introduction

Southwest Research Institute (SwRI) is the contractor for this Advanced Petroleum-Based Fuels - Diesel Emission Control (APBF-DEC) project, and technical guidance is provided by the APBF-DEC working groups. Caterpillar has provided 12-liter engines for the project, and Manufacturers of Emission Controls Association (MECA) has provided two exhaust emission control systems. Each emission control system includes a diesel particulate filter combined with SCR catalysts. Low-pressure-loop EGR systems were provided by STT-Emtech in Sweden, while Robert Bosch Corporation has provided the urea injection systems.

The plan is to optimize emissions performance with two different catalyst systems (Systems A and B), each comprised of DPF and urea SCR catalysts. After optimization, the emissions performance will be characterized with 4 different fuels - DECSE fuel with sulfur levels of 3, 8, and 15 ppm plus a BP refinery fuel with nominally 15 ppm sulfur. A limited test will be performed with DECSE 30 fuel (30 ppm sulfur). Emissions will be thoroughly

characterized for these tests, including unregulated emissions of interest plus some potentially problematic toxics emissions.

Following all the emissions tests with each system, the systems will be set up in a durability test cell, where they will undergo 6,000 hours of durability testing with emissions tests at the 2,000, 4,000, and 6,000-hour points.

Approach and Results

The first system has been set up in an emissions test cell at SwRI; a schematic of the system design is illustrated in Figure 1. A dual-leg exhaust system, employing two DPFs and SCR catalysts provided by the same manufacturer(s) was chosen to minimize the increase in back pressure and for other practical considerations.

The engine was first baselined for emissions and performance in an as-received condition using standard D2 fuel (of approximately 350 ppm sulfur content). Baselining consisted of running both the U.S. transient test cycle and the European OICA

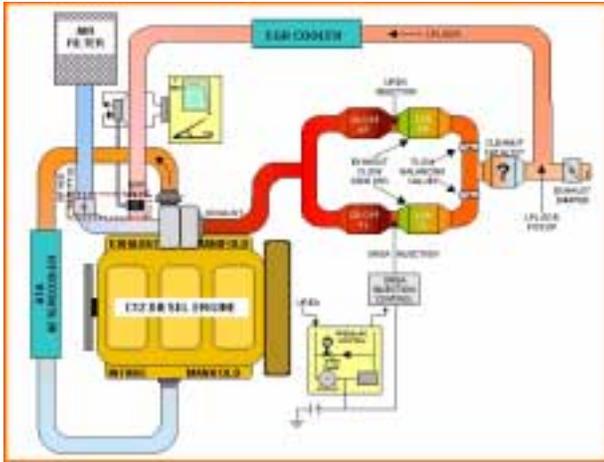


Figure 1. Test Setup

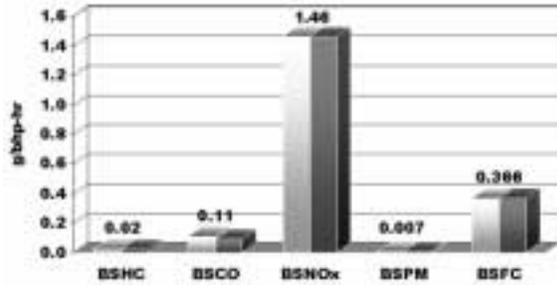


Figure 4. Transient Emissions - EGR* and DECSE 3 ppm Fuel - Two Hot Cycles

Data labels shown for only one of the cycles

* EGR - Low-Pressure-Loop EGR with CB-DPF

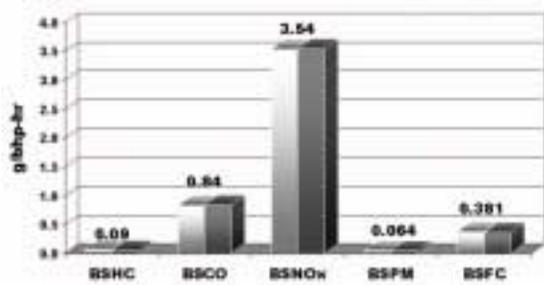


Figure 2. Transient Emissions - 350 ppm Certified 2D Fuel - Two Hot Cycles

* Data labels shown for only one of the cycles

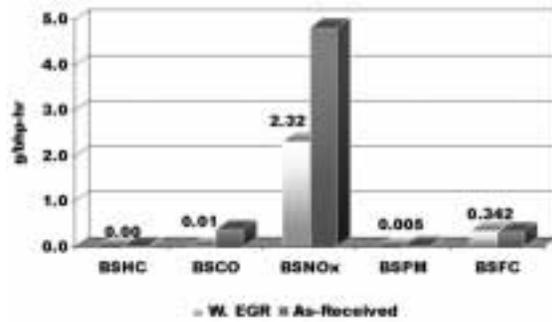


Figure 5. Steady-State Emissions Comparison - as Received with Certified 350 ppm Sulfur and with EGR*

Data labels shown for EGR case only

* EGR - Low-Pressure-Loop EGR with CB-DPF

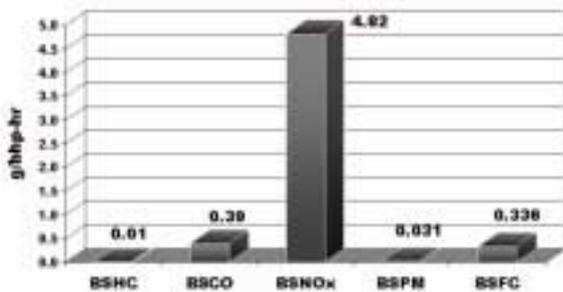


Figure 3. Steady-State Emissions - Hot Cycle - 350 ppm Certified 2D Fuel

cycle. Results for these tests are shown in Figures 2 and 3 respectively. Note that the baseline NO_x emissions are ~ 3.54 g/hp-hr and 4.82 g/hp-hr for the transient and steady-state, cycles respectively.

Next, the EGR system (along with the DPF for System A) was installed on the engine and calibrated for minimum engine-out NO_x while maintaining other parameters such as fuel consumption. (Note that the DPF was used with the EGR system so that the gases recirculated would be as free as possible from soot. Refer to Figure 1.) Results for the final EGR calibration on the transient cycle are shown in Figure 4, where engine-out NO_x has been reduced to 1.46 g/hp-hr, and PM (after the DPF) has been reduced to 0.007 g/hp-hr. Results for the OICA cycle are shown in Figure 5, where engine-out NO_x has been reduced to 2.32 g/hp-hr.

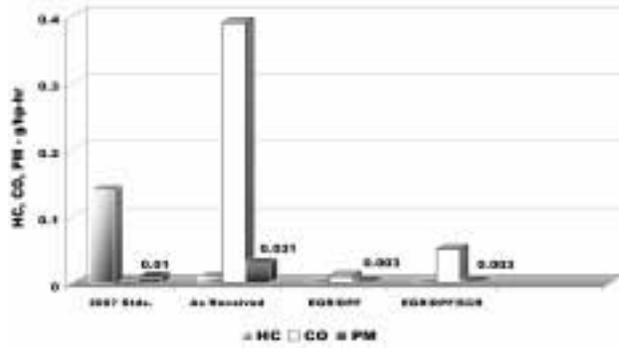


Figure 6. Steady-State Emissions (HC, CO and PM) Development and Progress

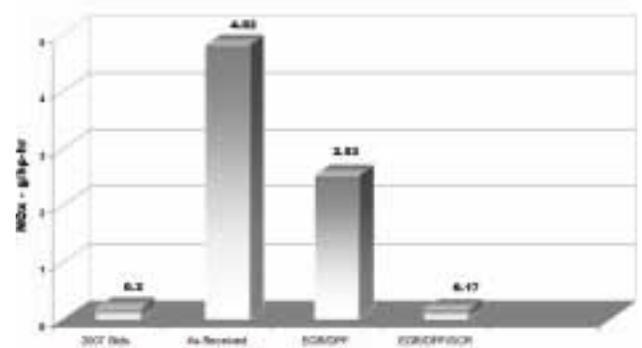


Figure 7. Steady-State Emissions (NO_x) Development and Progress

The next step was to add the urea SCR catalyst of System A and the urea injection systems. Optimization of the entire system, now including the SCR system, is still under way, but some promising results can be seen on the OICA cycle as shown in Figures 6 and 7, where the NO_x is reduced to 0.17 g/hp-hr, and PM is 0.003 g/hp-hr.

Conclusions

The calibration for System A will be completed very shortly at which time the emissions tests with the fuels matrix will be carried out. Following that, System A will be moved to the durability test cell while work will begin on System B to optimize and calibrate that system for minimum emissions.

F. Urea SCR System Evaluation with Emphasis on Unregulated Emissions

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Industry Participants: OMG-DMC2 Automotive Catalysts Division

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

- B. Fuel Property Effects on Exhaust Emission Control System Technology

Tasks

3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Evaluate the performance of urea selective catalytic reduction/diesel particulate filter (SCR/DPF) systems on a sports utility vehicle (SUV)-sized diesel engine
- Investigate the unregulated emissions from these systems utilizing realistic 2007 diesel fuels

Approach

- Tune system for steady-state and modal transient emissions performance
- Measure unregulated emissions during emissions evaluation of the SCR system using methods developed at Oak Ridge National Laboratory (ORNL) for the APBF-DEC project

Accomplishments

- Developed methods for measuring urea decomposition products
- OMG SCR, DPF and ARIS 2000 urea injection system installed
- Installed engine, dynamometer, controls, and data acquisition at the ORNL Network Technology Resource Center
- Preliminary data from modal testing obtained to validate measurement techniques

Future Directions

- Continue to evaluate SCR catalyst 1 with ARCO ECD fuel and BP fuel (from APBF-DEC)
- Obtain steady-state regulated and unregulated emissions
- Obtain regulated emissions on modal transients
- Analyze data reduction and communicate results to partners
- Repeat with Catalyst 2

Introduction

Urea SCR has emerged as a promising technology for the reduction of oxides of nitrogen (NO_x) from compressed ignition direct injection (CIDI) engines. Several groups have demonstrated emissions levels at or near the 2007 heavy-duty engine emission standards as well as Tier 2 emission levels for light-duty vehicles. The technology uses a urea solution injected into the exhaust as a source of ammonia, which then reacts with NO_x on the catalyst to reduce NO_x to diatomic nitrogen (N_2).

In an ideal case, the urea dissociates completely in the exhaust to ammonia and carbon dioxide (CO_2), as shown in Figure 1.

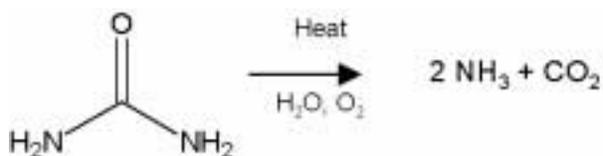


Figure 1. Ideal Formation of NH_3 from Urea

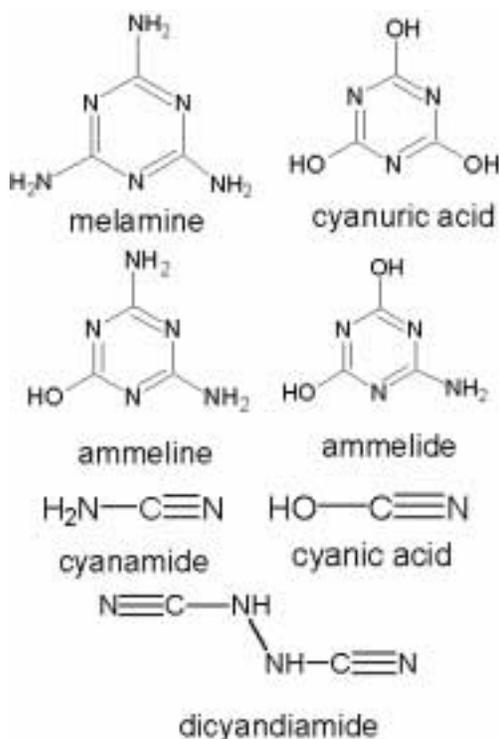


Figure 2. Chemical Structures of Several Urea Decomposition Products

However, many other urea decomposition products are possible; Figure 2 shows a selection of compounds that have been detected in exhaust from an engine equipped with an SCR system.

These and other unregulated emissions, such as ammonia (NH_3) and N_2O , are important to characterize both for potential health effects issues and as an indicator of catalyst system performance.

In this report, we describe an ongoing series of experiments to examine the performance and unregulated emissions from SCR/DPF systems.

Approach

A combined SCR-DPF system, provided by OMG-DMC2, is being investigated at the ORNL Fuels, Engines, and Emissions Research Center (FEERC). Figure 3 shows a schematic of the system. The oxidation catalyst provides heat and helps to convert NO to NO_2 , as the SCR prefers a 50:50 ratio of $\text{NO}:\text{NO}_2$. Unlike another SCR-DPF system studied earlier [2], this system has the DPF downstream of the SCR catalyst. This arrangement allows the exhaust heat to be conserved to keep the SCR catalyst at high conversion levels. The engine is a Cummins B5.9 that is equipped with exhaust gas recirculation (EGR). Although this is a medium-duty engine, the exhaust flows and temperatures are similar to smaller, high-speed CIDI engines expected to be in service in SUVs in the near future. Figure 4 is a photograph of the engine and system installed at the FEERC.

The urea injection system is an ARIS 2000 system which has been described elsewhere [2]. This system can be programmed a priori to follow

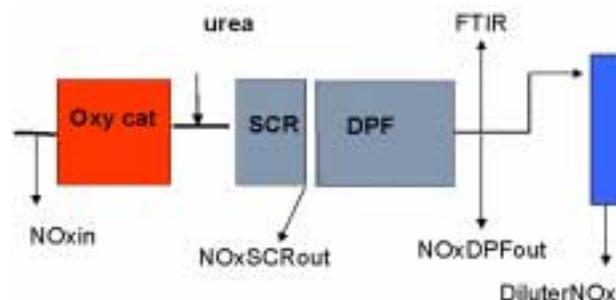


Figure 3. Schematic of the SCR-DPF System Used in this Study



Figure 4. Photograph of the SCR-DPF System Installed on a Cummins B5.9 Engine

transients, but it is not capable of true transient operation. Thus, for these experiments, steady-state operation will be used for the majority of unregulated emissions testing. In addition, programmed transients will be done to see if there are any unusual emissions due to transient operation.

Two SCR formulations provided by OMG-DMC2 will be evaluated, operating on two different fuels. The fuels were selected to represent possible refinery fuels that will be available in 2007. Arco ECD-1 is a 15 ppm sulfur fuel representative of a hydro-treated fuel. In addition, the BP refinery fuel, a hydro-cracked fuel and also 15 ppm sulfur, will be used in this study.

Several of the modes from the AVL 8 mode test were run. A micro-dilution system was used to dilute the exhaust for particulate matter (PM) and hydrocarbon (HC) measurements. Bag HCs were analyzed using an Entech Preconcentrator coupled to a Hewlett-Packard gas chromatography-mass spectrometer (GC-MS) system. Raw exhaust was collected in impingers containing a 70% solution of isopropanol in water for measurement of urea decomposition products. The impinger solutions were analyzed by capillary electrophoresis equipped with ultraviolet (UV) detection. PM samples were collected on 70 mm Pallflex Teflon-coated quartz fiber filters. A Fourier Transform Infrared (FTIR) and photoacoustic analyzer (PAS) were used to measure N_2O and NH_3 slip. An in-house UV

absorption spectrometer was also implemented to get higher speed measurements of NH_3 .

Preliminary Results

This project is ongoing, so only some preliminary results from the first SCR formulation using the ARCO ECD-1 fuel are available. It was determined after these experiments that a malfunction in the urea injection system was causing excess reductant injection, so the results represent an upset condition, rather than proper operation. Unfortunately, our FTIR and PAS were unable to detect the excess NH_3 , so the extent of the problem was only realized after implementation of the UV system. It is believed that the excess NH_3 was being retained in the sampling systems for the FTIR and the PAS, and thus was not able to be measured by these instruments.

Figure 5 shows NO_x conversion results for the SCR and SCR-DPF combination at both a high-speed, high-load point (Mode 8) and a low-speed, high load point (Mode 4.) Note that the lower space velocity resulted in better conversion. We now believe this was due to the higher NO_x level of Mode 4. More of the excess NH_3 was able to react with the higher NO_x , resulting in better NO_x conversion. Excess NH_3 can often result in poor NO_x conversion because the NH_3 is converted to NO_x either by the DPF or the internal catalyst in the chemiluminescence analyzer used to measure NO_x .

After implementation of the UV instrument, the urea injection system could be tuned to limit NH_3

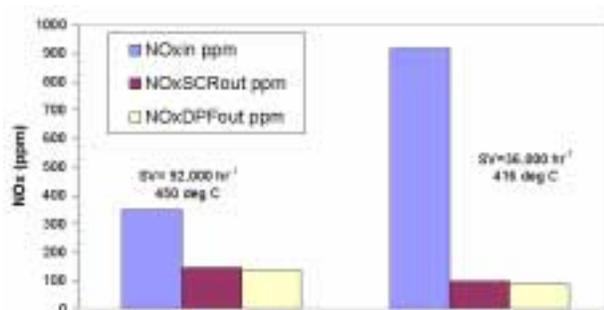


Figure 5. NO_x in and out of the system for AVL Mode 8 and Mode 4. Note that 99% NO_x conversion was achieved for Mode 8 after tuning injection system for low NH_3 slip.

slip. A re-check of Mode 8 showed 98-99% conversion under the low NH_3 slip conditions.

Unregulated emissions were collected during this preliminary phase of the research. Impinger samples showed an excess of cyanic acid (see Figure 2) being generated during several of the modes. We believe this was due to the excess urea solution being injected. Bag HC speciation of the exhaust also indicated the formation of some unusual species. Figure 6 shows the ion chromatograms of exhaust samples taken during Mode 8 with and without urea injection. The particular ion chosen, $m/z = 30$, is the marker for alkyl nitrate species, and thus each of the peaks corresponds to a different alkyl nitrate compound. While there is a small amount of alkyl nitrate being emitted from the DPF, the third trace shows a very large amount of a low molecular weight alkyl nitrate being generated by the SCR. This is very likely CH_3NO_3 , methyl nitrate. Methyl nitrate is significant because it binds NO_x such that the standard chemiluminescence detector is unable to detect NO_x , and it is also a very reactive compound. As with the previous results, the generation of the methyl nitrate is believed to be due to the over-injection of urea solution and subsequent oxidation of cyanuric acid or another compound on the SCR catalyst.

While the preliminary results were unusual due to the excess of urea injected, the methods we have developed for unregulated emissions analysis worked very well, and we expect to have much better success in subsequent experiments with a properly functioning urea injection system.

Further work will focus on completion of the study using the two SCR formulations and the two fuels. Because of the unusual results with excess urea injection, we plan to study more mild excursions from normal operation. An important finding from this work will be the threshold of excess urea injection above which the unusual chemistry occurs.

Summary

An SCR-DPF system has been installed and operated on a turbocharged, direct-injected diesel engine. Preliminary data on the system has been acquired, showing excellent NO_x conversion under normal operation. Under conditions of excess urea

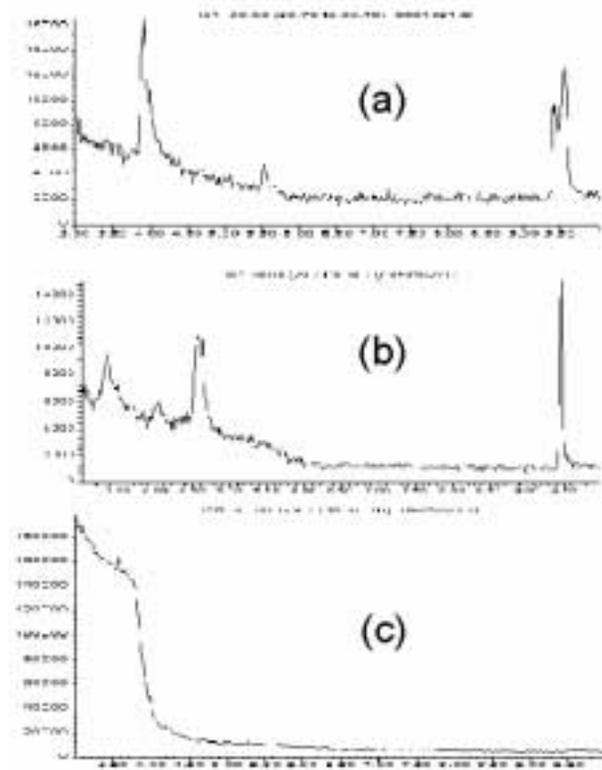


Figure 6. GC-MS ion chromatograms ($m/z = 30$) of exhaust from a) DPF with no urea injection; b) DPF with urea injection; c) SCR with urea injection. The saturated signal in (c) indicates a large amount of alkyl nitrate formation, most likely methyl nitrate.

injection, unusual species formed in the exhaust. The methods developed for the measurement of these species proved successful. The study will be completed this year.

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G. The Impact of Oxidation Catalysts on Diesel Engine Emissions

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Main Subcontractors: Coordinating Research Council, Inc., Alpharetta, Georgia; Southwest Research Institute, San Antonio, Texas

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

E. Toxic Emissions

Tasks

3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Assess the impact of diesel oxidation catalysts (DOC) in altering the particulate and gaseous emissions characteristics of a state-of-the-art light-duty diesel engine
- Test multiple diesel oxidation catalysts to characterize engine-out and tailpipe diesel emission characteristics
- Evaluate an engine/oxidation catalyst technology combination that with appropriate particulate trap technology will meet Tier 2 emission standards, but only explore the effect of the DOC

Approach

- Task 1 - Catalyst Procurement. Catalyst suppliers will provide diesel oxidation catalysts for evaluation. These catalysts will be close-coupled to the engine, and at least three advanced catalysts will be obtained for the study.
- Task 2 - Catalyst Degreening and Stabilization. Each catalyst will be installed on a vehicle operated for 4,000 miles to achieve stable performance.
- Task 3 - Equipment Setup and Measurement Repeatability Verification. Theoretical analysis will be conducted to determine particle losses that may occur in the particulate sampling system for particle sizes ranging from 10 nanometers to 1 micron. Experimental loss analysis will also be performed in the micro-dilution tunnel using solid particle standards. Repeatability of all particulate and gaseous measurements will be determined in this task.
- Task 4 - Catalyst Evaluations with Low Sulfur Fuel. Evaluate three diesel oxidation catalysts using a light-duty 1999 Mercedes Benz C220 CDI vehicle equipped with a diesel-powered 2.2 liter OM611 engine. The vehicle will use a fuel expected to be representative of the 2007 federal specification. The fuel will be procured with a sulfur content of approximately 10 parts per million (ppm). Test cycles

will be three steady-state conditions, the Federal Test Procedure, and the US06 to achieve exhaust temperatures ranging from 150°C to 450°C.

- Task 5 - Chemical and Physical Characterization of Exhaust Emissions. Regulated gaseous emissions will be sampled and measured according to appropriate Environmental Protection Agency protocols as identified in the Code of Federal Regulation. In addition to dilute exhaust samples, second-by-second raw exhaust concentrations will be recorded prior to the close-coupled catalyst to assure consistent operation of the vehicle. Concurrent with the collection of gaseous emissions, a variety of particulate samples will be collected for physical and chemical characterization. Total particulate mass; volatile organic fraction of particulate; sulfate fraction of particulate; trace metals and inorganic ash; elemental and organic carbon particulate content; poly-aromatic hydrocarbons (PAHs), nitro-PAHs, and oxy-PAHs; PM_{2.5} mass fraction, PM₁₀ mass fraction, and particulate matter (PM) size distribution will each be measured for characterization of exhaust particulate matter upstream and downstream from the diesel oxidation catalyst. Speciation of gaseous emissions will also be determined, including C1 to C4 species, C5-C12 species, benzene and toluene, and aldehydes and ketones upstream and downstream of the catalyst. SO₂ to SO₃ (sulfur oxides) conversion over the catalyst will also be determined.
- Task 6 - Statistical Analysis. The experimental design for the project will be established to determine significant differences between engine-out and catalyst-out emission levels and characteristics for each test cycle on the test fuel.

Accomplishments

- Final test fuel obtained that meets 2007 federal specification of 15 ppm sulfur was obtained
- Experimental design has defined the number of replicates required for each test condition
- Oven-aged test catalysts provided by Manufacturers of Emissions Controls Association (MECA)
- Catalysts stabilized by vehicle operation
- Test vehicle (Mercedes Benz C220 CDI vehicle equipped with a diesel-powered 2.2 liter OM611 engine) procured for the project
- Baseline emissions established and emissions testing on 2 catalysts completed
- Basic PM characterization conducted on baseline catalysts and first two test catalysts

Future Directions

- Conduct emissions tests on third catalyst (highest metal loading)
- Conduct chemical analyses on exhaust samples

Introduction

Today's advanced technology diesel engines typically include four valves per cylinder, common rail injection, and turbocharging. However, diesel engines have a disadvantage of higher particulate emissions compared to gasoline engines. In addition, these particulates may contain unburned fuel species or products of combustion, which are undergoing scrutiny as potential air toxics. Diesel exhaust also contains gaseous hydrocarbon species that may be potential air toxics.

To reduce particulate emissions from diesel engines, aftertreatment manufacturers are developing several control technologies, including particulate filters, catalytic traps, and oxidation catalysts. In addition, technologies employing plasma and microwave techniques are being explored. These technologies have the potential to not only reduce the particulate mass loading, but also to alter the other characteristics of diesel exhaust. For example, an oxidation catalyst may be effective in oxidizing or reducing some of the gaseous organics in the exhaust or the liquid organic species deposited on the

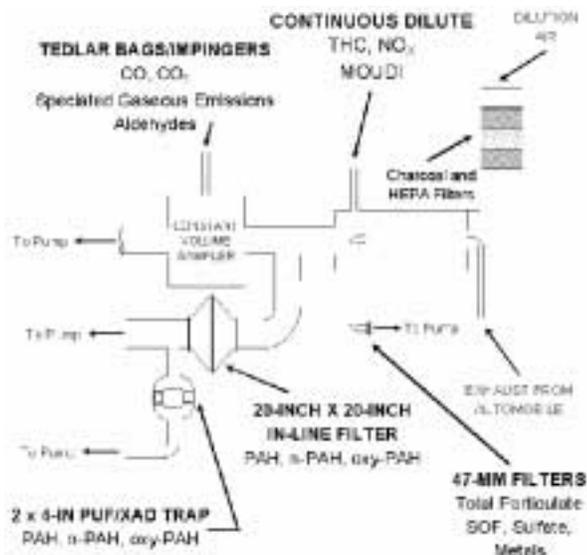


Figure 1. Sampling System for DOC Emissions Characterization



Figure 2. Mercedes Benz C220 CDI Vehicle Equipped with a 2.2L OM611 Diesel-Powered Engine

particulate. Therefore, these particulate control devices may beneficially alter the overall emissions characteristics of the diesel vehicle.



Figure 3. Installed Diesel Oxidation Catalyst Configuration

Approach

This project is being conducted with collaborative funding and technical support from the Advanced Vehicle Fuel Lubricant (AVFL) Committee of Coordinating Research Council, Inc. (CRC). MECA is providing in-kind technical services and catalyst materials to support the work. The National Renewable Energy Laboratory is coordinating specification and acquisition of the test fuel and selection of the catalysts in concert with other related DOE research projects. The experimental program is being conducted through a contract with Southwest Research Institute (SwRI) in their Department of Emissions Research.

The detailed approach for accomplishing the project objectives is described in the corresponding section above. The emission sampling system used by SwRI is depicted in Figure 1. The test vehicle is illustrated in Figure 2. A sample of the installed test catalyst configuration is shown in Figure 3.

Conclusions

At the time of this report the test program results are considered preliminary and summary conclusions have not been defined.

IV. VEHICLE TEST AND EVALUATION

A. The Emissions Impacts of Various Fuels on a CIDI Vehicle

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This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

B. Fuel Property Effects on Exhaust Emission Control System Technology

E. Toxic Emissions

Tasks

3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objective

- Quantify the effects of advanced petroleum fuel oxygenate blends on the emissions of a vehicle powered by a state-of-the-art CIDI engine (OM611).

Approach

- Six fuels will be evaluated for tailpipe exhaust emissions from a European Mercedes Benz C220D series vehicle following the chassis dynamometer portion of the Federal Test Procedure (FTP) and the US06 aggressive driving cycles.

Accomplishments

- The matrix of test fuels was approved by the U.S. Department of Energy. It includes advanced oxygenate blends, advanced fuel containing ethanol, and a fuel blend containing water.
- Testing was delayed pending the availability of a special base fuel that is a refinery produced prototype of 2007 U.S. ultra-low-sulfur diesel fuel.

Future Directions

- Evaluate the effects of fuel blends containing oxygenated materials in an advanced CIDI-powered vehicle that has advanced emission control devices such as NO_x adsorption and diesel particulate filter technologies.

Introduction

Exhaust emission reductions have been demonstrated in many previous studies using alternative and reformulated diesel fuels. In previous

investigations related to this project, exhaust emissions were determined in a Mercedes Benz "C" Series European vehicle (C220D) for a series of advanced petroleum-based fuels. The vehicle is powered by the OM611 engine, which has a



Figure 1. Mercedes Benz C220D

displacement of 2.2L and the following characteristics: direct-injection, four valves per cylinder, turbocharging and intercooling, high-pressure common rail fuel injection system with pilot injection, exhaust gas recirculation, and intake port cut-off. According to the vehicle manufacturer, the emission control system of the C220D vehicle includes one catalytic converter close to the engine with a volume of 2.1 L, and an additional underbody catalytic converter with a volume of 1.8 L. Both converters have a platinum coating on a zeolite substrate and provide oxidation of hydrocarbons and CO with a slight reduction in NO_x (i.e., a "lean- NO_x " catalyst). The converter closest to the engine has an internal by-pass so that the underbody converter is supplied with hydrocarbons to assist in an additional slight reduction in NO_x . Figure 1 is a photograph of the Mercedes Benz C220D vehicle.

In the previous investigations, none of the fuels tested in the C220D vehicle allowed it to meet EPA Tier 2 exhaust emission standards (note: this vehicle was not designed to meet the EPA Tier 2 standards). With respect to test cycle severity, the US06 was the most severe, followed by the FTP and then the European cycles. Overall, the results showed the benefit in PM reduction for the oxygenated fuel over the FTP and European cycles. No statistically significant emissions reductions were observed over the US06 aggressive driving cycle. The fuel blend containing 15% di-methyl maleate (DMM) consistently produced the lowest PM emissions; however, a slight increase in NO_x was observed.

DMM15 fuel consistently had the lowest levels of volatile organic fraction (VOF). Fuel economy for the DMM15 fuel ranged from 8 to 11% less than the baseline fuel (2D).

Approach

This project will include exhaust emission evaluations of a Mercedes-Benz C220D equipped with the OM611 engine. This four-valve-per-cylinder engine is turbocharged and intercooled, and includes a high pressure, common rail fuel injection system, exhaust gas recirculation, pilot injection and intake port cut-off. This vehicle is equipped with "lean- NO_x " catalyst technology, which relies on low-sulfur fuel to be effective. The vehicle will be tested using the following six fuels:

- BP15 Fuel (prototype 2007 U.S. ultra-low-sulfur diesel fuel)
- BP15 Fuel + tripropylene glycol monomethyl ether (TPGME) @ 7% oxygen
- BP15 Fuel + TPGME @ 3.5% oxygen
- BP15 Fuel + di-butyl maleate @ 7% oxygen
- BP15 Fuel + 10% ethanol
- BP15 Fuel based water emulsion

All six fuels will be evaluated over the chassis dynamometer portion of the Federal Test Procedure (FTP) and the US06 aggressive driving cycles. All test cycles will be conducted in triplicate.

Testing will utilize a Horiba 48-inch single-roll chassis dynamometer. This dynamometer electrically simulates inertia weights up to 12,000 pounds over the FTP-75 (up to 7,000 pounds for vehicles capable of following the US06 driving trace), and provides programmable road load simulation of up to 125 hp continuous at 65 mph (300-hp momentary duty at 65 mph). Southwest Research Institute (SwRI) will use a Mears Model to calculate a road load curve for the vehicle. This model requires coastdown data from drive and non-drive axles. A total of three coastdowns will be conducted on each axle, and the average results will be used as input for the Mears Model. The resulting calculated road load curve coefficients will be entered as the target "a", "b", and "c" values for use during the Horiba Road Load Derivation routine. With this routine, coastdowns are conducted with the

vehicle on the chassis dynamometer to determine appropriate chassis dynamometer load coefficient settings. Vehicle equivalent test weight will be the measured curb weight of the vehicle with a 40 percent fuel fill plus 300 pounds.

Dilute exhaust emission sampling will utilize a positive displacement-type constant volume sampler (CVS). An 18-inch diameter by 16-ft. long stainless steel dilution tunnel will be used in conjunction with the CVS to maintain an average tunnel sampling zone temperature of 110°F, with the maximum temperature not to exceed 125°F during the standard Federal Test Procedure. Nominal CVS flow rate will be 600 cubic feet per minute (cfm). A constant-speed cooling fan of 5,000 cfm capacity will be used in front of the vehicle during operation.

Regulated exhaust emissions (total hydrocarbons, carbon monoxide, oxides of nitrogen, and particulate matter) and carbon dioxide will be sampled and measured in a manner consistent with Environmental Protection Agency protocols for light-duty emission testing as given in the Code of Federal Regulations. Proportional dilute exhaust gas samples will be collected in Tedlar bags for analysis of carbon monoxide and carbon dioxide. Total hydrocarbons and oxides of nitrogen will be measured continuously from the dilution tunnel. Concurrently, a proportional sample of the dilute exhaust will be drawn through Pallflex T60A20 fluorocarbon-coated glass fiber filters for determination of particulate matter. Filter samples will be analyzed by direct filter injection gas chromatography (DFI/GC) to determine the particulate VOF and lubricating oil contribution to VOF. Exhaust constituents will be analyzed as specified below:

Constituent	Analysis Method
Total Hydrocarbon	Heated Flame Ionization Detector
Carbon Monoxide	Non-Dispersive Infrared Analysis
Carbon Dioxide	Non-Dispersive Infrared Analysis
Oxides of Nitrogen	Chemiluminescent Analysis
Particulate Matter	Gravimetric
Volatile Organic Fraction of PM	Direct Filter Injection Gas Chromatography
Oil Fraction of VOF	Direct Filter Injection Gas Chromatography

Appropriate statistical techniques will be used to determine differences between the six fuels. Analysis of variance will determine whether the average response of the six fuels is statistically different. All comparison tests will be made at the 5% level of significance.

Results

The project was delayed pending the availability of the BP15 Fuel. Testing will be completed in early 2003.

B. EC-Diesel Technology Validation Project

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Subcontractors: West Virginia University, WV; Desert Research Institute, Reno, NV

This project addresses the following OTT R&D Plan barriers and tasks:

Barriers

- B. Fuel Property Effects on Exhaust Emission Control System Technology
- C. Emission Control System Degradation
- E. Toxic Emissions
- F. Ultra-fine Particles

Tasks

- 3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objectives

- Compare exhaust emissions from vehicles fueled with EC-Diesel (ECD) and California Air Resources Board (CARB) diesel fuels.
- Evaluate the performance, emissions, and durability of the vehicles retrofitted with catalyzed particle filters and fueled with ECD over twelve or more months of service.
- Collect fuel consumption, maintenance, reliability, and operating cost data for the participating vehicle fleets and compare to control vehicles fueled with CARB diesel fuel.
- Chemically characterize the emissions from a select subset of vehicles in the fleets to compare the effects of ECD and ECD-1, with and without diesel particle filters, to CARB diesel fuel.

Approach

- Work with government-industry working group that was established in FY01 to select vehicle fleets for participation in the project.
- Design test matrix for regulated and unregulated emissions testing for the second round of vehicle tests in the winter of 2001.
- Compare first and second round of emissions test results.
- Objectively analyze vehicle performance and emissions data for both fuels, and draw conclusions.
- Objectively analyze the unregulated emissions results for the fuel and aftertreatment combinations, and draw conclusions.

Accomplishments

- Second round test results were published in an SAE (Society of Automotive Engineers) technical paper (2002-01-0433). The results in the paper include emissions and vehicle performance data. A technical presentation was made at the 2002 SAE World Congress highlighting the results in the paper.
- A final data report documenting the detailed vehicle performance results from the Ralphs grocery fleet was published.
- Results from a portion of the chemical characterization, including particle sizing, inorganic ions and elements, benzene, light olefins, toluene, ethyl-benzene, xylene isomers (BTEX), and ethene data, have been published in an SAE technical paper (2002-01-0432) and presented at the 2002 SAE World Congress.

Future Directions

- Additional results, including polycyclic aromatic hydrocarbons (PAH), nitro-PAH (n-PAH), and 1,3-butadiene, from the chemical characterization will be published in FY03.
- Further testing is needed to examine the capabilities and limitations of passive diesel particle filters in colder climates and in older vehicles.

Introduction

ARCO, a BP company, has developed two new diesel fuels called Emission Control Diesel (ECD) and Emission Control Diesel-1 (ECD-1). Both fuels have sulfur contents of less than 15 ppm. The ECD fuel has an aromatics content of 10% and a cetane number of 60. The ECD-1 fuel, BP's commercial product, has an aromatics content of 22% and a cetane number of 50.

Catalyzed diesel particle filters have been shown to operate more efficiently as diesel fuel sulfur content is decreased (1,2,3). Ultra-low sulfur diesel fuels expand the filter regeneration temperature window, improving particulate matter removal for a wide range of engine operating conditions.

A one-year technology validation project was conducted to evaluate ECD and catalyzed diesel particle filters on diesel vehicle fleets in Southern California. The fuel's performance, impact on engine durability and vehicle performance, and emission characteristics were evaluated and compared to conventional CARB diesel fuel.

Several vehicles from the project were selected for detailed exhaust chemical characterization. The vehicles were operated on CARB and ultra-low sulfur diesel fuels, with and without diesel particle

filters. The results from the exhaust characterization were compared, using the CARB diesel fuel as a normative baseline.

Approach

Seven Southern California heavy-duty diesel fleets were selected to participate in the ECD Technology Validation Project. The fleets contained a set of nominally identical vehicles that participated in the project. Within each fleet, a number of vehicles were selected as control vehicles fueled with CARB diesel fuel and no aftertreatment. Of the remaining vehicles, all were fueled exclusively with ECD for the twelve-month project. Several of the ECD-fueled vehicles were operated without aftertreatment. The final set of ECD fueled vehicles were retrofit with either Johnson Matthey's Continuously Regenerating Technology (CRT™) or Engelhard's catalytic soot filter (DPX™).

Both the DPX and CRT are passively regenerated diesel particle filters. The filters replaced the existing muffler. No engine modifications were made to the vehicles with the DPX or CRT filters.

Results

Two rounds of emission testing were performed to evaluate the performance of the filters over the

twelve-month test period. The fleet vehicles operated in typical duty cycles throughout the performance period. The filters were not serviced between the first and second rounds of emissions testing. Emission test results showed the filters were effective at removing ~90% of the PM after twelve months of operation (4).

The Ralphs grocery fleet was selected for evaluation of operating cost, maintenance, and fuel economy. Total operating costs were comparable for the fleet, regardless of fuel type or presence of aftertreatment (4). Twenty vehicles participated in the project, with five vehicles operated on CARB diesel fuel (control vehicles). The fifteen remaining vehicles were operated on ECD fuel. Five of the fifteen were operated without aftertreatment. Ten vehicles were retrofit with diesel particle filters, five each with the Johnson Matthey CRT and the Engelhard DPX. No difference was observed in the fuel economy for the vehicles operating with DPFs compared to the CARB diesel vehicles (Figure 1).



Figure 1. Average Fuel Economy for Grocery Trucks with and without Diesel Particle Filters

One of the Ralphs grocery trucks was selected for exhaust chemical characterization. The particulate matter was collected with size selective cyclones to give a rough approximation of the size. The PM was divided into three categories – total particulate matter (TPM), PM₁₀ (all PM less than 10 μm), and PM_{2.5} (all PM less than 2.5 μm). Results show that the TPM, PM₁₀, and PM_{2.5} emissions are similar for the CARB and ECD-1 fuels. The aftertreatment reduced the TPM, PM₁₀, and PM_{2.5} emissions by ~90% (Figure 2).

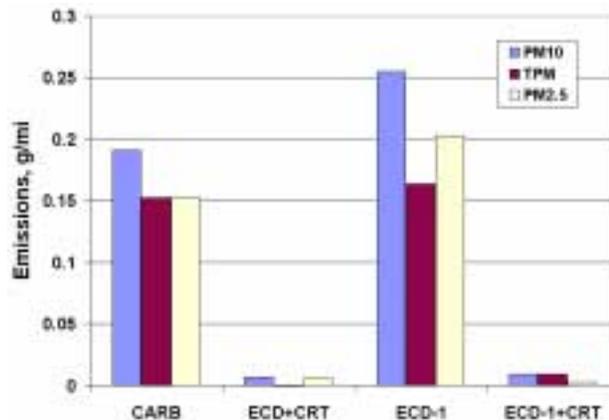


Figure 2. TPM, PM₁₀, and PM_{2.5} Emissions from a Grocery Truck Operating on CARB and ECD-1 without Aftertreatment, and ECD and ECD-1 with CRT

The ‘CARB’ and ‘ECD-1’ captions signify the grocery truck operating on CARB or ECD-1 diesel fuel without aftertreatment, respectively. The ‘ECD+CRT’ and ‘ECD-1+CRT’ represent the grocery truck operating on ECD or ECD-1 fuel and retrofit with the CRT particle filter.

Light olefins are important precursors for ozone formation. The CARB and ECD-1 diesel fuels without aftertreatment have similar emissions, while the CRT reduced the emissions by ~80% (Figure 3).

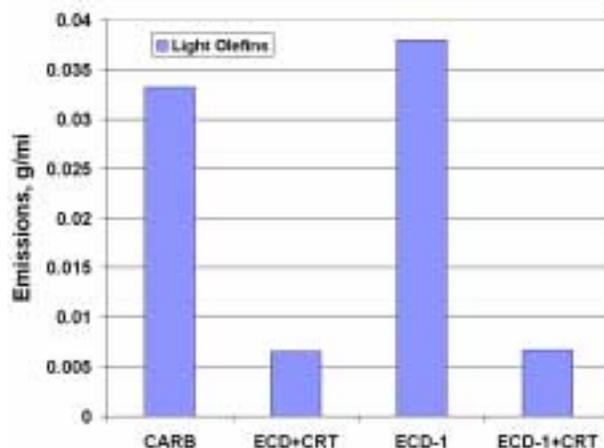


Figure 3. Light Olefin Emissions from a Grocery Truck Operating on CARB and ECD-1 without Aftertreatment, and ECD and ECD-1 with CRT

Conclusions

Several heavy-duty diesel fleets have been retrofitted with diesel particle filters. Two rounds of emissions testing have been completed showing that the filters are effective at removing PM, HC, and CO emissions after twelve months of continuous use. Vehicles operating on the filters did not have a significant fuel economy penalty, compared to vehicles operating on conventional diesel fuel. The filters were effective at reducing unregulated emissions, such as PM₁₀, PM_{2.5}, and light olefins.

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1. LeTavec, C., Uihlein, J., Vertin, K., Chatterjee, S., Wayne, S., Clark, N., Gautam, M., Thompson, G., Lyons, D., Hallstrom, K., Chandler, K., Coburn, T., "Year-Long Evaluation of Trucks and Buses Equipped with Passive Diesel Particulate Filters", SAE Technical Paper No. 2002-01-0433, 2002.

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V. SUPPORTING RESEARCH

A. Investigation of the Combustion and Soot-Formation Characteristics of Oxygenated Diesel Fuels

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This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

- A. Fuel Property Effects on Engine Emissions and Efficiency
- F. Ultra-fine Particles

Tasks

- 2. Fuel & Lubrication Properties - Engine-Out Emissions

Objectives

- Enhance fundamental understanding of how diesel fuel oxygenates affect mixing, combustion, and emissions-formation processes within the engine cylinder.
- Determine why some oxygenates are better than others at reducing particulate matter emissions from compression ignition direct injection (CIDI) engines.
- Use new knowledge to help identify a "short list" of oxygenate molecules that show particular promise for delivering excellent engine performance with minimal emissions.
- Feed back new fundamental knowledge to engine manufacturers, fuel suppliers, and other stakeholders so that engine design and fuel formulation can be used together in an optimal manner to meet future emissions and efficiency goals.

Approach

- Task 1 Complete detailed natural luminosity (NL) imaging study of combustion of two oxygenated fuels and one reference fuel in Sandia/Caterpillar Optical Research Engine (SCORE) laboratory. Fuels are formulated such that oxygenate molecular structure is the only significant difference between two oxygenated fuels; other properties such as oxygen content, combustion phasing, operating conditions, and adiabatic flame temperature are explicitly matched. Oxygenates under study are di-butyl maleate (DBM) and tri-propylene glycol methyl ether (TPGME).
- Task 2 Derive a mathematical relationship between NL signal and soot concentration at a point within the engine cylinder.
- Task 3 Use mathematical relationship developed in Task 2 along with known properties of soot, fuels, and imaging system to determine whether spatially integrated natural luminosity (SINL) can be used to rank oxygenates based on their ability to reduce in-cylinder soot concentrations.
- Task 4 Verify results from Tasks 1-3 with laser-induced incandescence (LII) measurements in the Diesel Combustion Simulation Facility (DCSF).
- Task 5 Attempt to determine reasons why one oxygenated test fuel produces significantly more soot than another, even when all other variables are matched.
- Task 6 Initiate and demonstrate accelerator mass spectrometry (AMS) measurement capabilities in the SCORE laboratory. Obtain information about chemical-kinetic pathways underlying enhanced soot-reduction potential of one oxygenated fuel relative to another.
- Task 7 Analyze results and report findings to collaborators in industry, academia, and national laboratories. Publish in open literature to broadly disseminate results and conclusions.

Accomplishments

- Completed all tasks. Some highlights:
 - Quantified relationship between NL signal and local soot volume fraction.
 - Conducted detailed analysis to show that, under the present conditions, peak SINL can be used as a conservative method to rank the test fuels based on their ability to reduce the average in-cylinder soot volume fraction.
 - Discovered that fuel containing TPGME oxygenate was significantly more effective at reducing in-cylinder soot than fuel containing DBM oxygenate.
 - Found that both oxygenated fuels significantly reduce in-cylinder soot relative to the non-oxygenated reference fuel.
 - Observed same rank-ordering of test fuels in LII imaging experiments conducted in DCSF.
 - Measured flame lift-off lengths in DCSF to show that differences in air entrainment are not large enough to account for observed differences in soot production between the oxygenated fuels.
 - Conducted a double-distillation analysis of DBM oxygenate to reveal evidence of polymerization and/or thermal decomposition before complete vaporization. This finding may help account for its relatively higher soot production and may provide a warning sign for injector deposit formation problems with the DBM oxygenate.
 - Added capability to use AMS diagnostics in SCORE laboratory to track carbon atoms in specific bond positions from the fuel molecule, through the combustion event, to particulate and gaseous emissions.

Future Directions

- Measure test fuel lift-off lengths in optical engine and compare to results from DCSF. Multiple-jet and jet-wall interactions that are absent in DCSF may be important in engine.
- Measure test fuel soot distributions in DCSF using a quantitative laser-extinction diagnostic. Fuel-bound oxygen may be more effective at reducing soot than oxygen entrained from charge air.
- Continue AMS experiments with oxygenates and expand scope to include other fuel constituent molecules. Results will help identify links between fuel molecular structure and particulate/gaseous emissions from CIDI engines.
- Initiate development of in-cylinder NO_x measurement capabilities to study combined effects of fuels and operating conditions on NO_x evolution.

Introduction

Blending oxygen-containing compounds ("oxygenates") with diesel fuel can lead to reduced soot and nitrogen oxides (NO_x) emissions, as well as reduced fuel consumption. The detailed mechanisms that cause such reductions are not well understood. This project is focused on understanding why certain oxygenates are better than others at reducing the amount of soot produced by CIDI engines.

Approach

The SCORE laboratory shown in Figure 1 features a single-cylinder version of a modern-technology, Caterpillar 4-stroke DI diesel engine that has been modified by Sandia to provide extensive optical access into the combustion chamber [1]. The optical engine is based on the Caterpillar C-10 platform used in heavy-duty trucking. A schematic of the optical engine is shown in Figure 2. The large window in the piston bowl enables combustion processes within the engine to be imaged during operation. Specifications of the optical engine are provided in Table 1.

In-cylinder images of NL and spray development were acquired and coupled with measurements of cylinder pressure and injected fuel quantity. The NL image sequences show the evolution of regions of high soot concentration and temperature throughout the combustion event. The spray-development images provide verification that the experimental fuels do not degrade fuel-injection system performance over time. The cylinder pressure and injected quantity measurements provide information about heat-release rates and engine efficiency, respectively.

Table 1. Specifications of the Sandia/Caterpillar Optical Research Engine

Production engine type	6-cyl. Caterpillar C-10
Research engine type	1-cyl. version of C-10
Cycle	4-stroke CIDI
Valves per cylinder	4
Ignition assist (not used)	In-cylinder glow plug
Bore	125 mm
Stroke	140 mm
Peak cylinder pressure	14.0 MPa
Intake valve open	32° BTDC exhaust
Intake valve close	153° BTDC compression
Exhaust valve open	116° ATDC compression
Exhaust valve close	11° ATDC exhaust
Connecting rod length	225 mm
Connecting rod offset	None
Bowl diameter	90 mm
Bowl depth	16.4 mm
Swirl ratio	0.59
Displacement per cyl.	1.72 liters
Compression ratio*	11.3:1
Simulated compr. ratio	16.0:1

*TDC temperature, density, and pressure in the production engine are matched in the optical engine by preheating and boosting the pressure of the intake air.

Three test fuels were formulated for this work: one non-oxygenated reference fuel (denoted CN80) and two oxygenated fuels. Overall oxygen content was matched for the two oxygenated test fuels. The two oxygenate molecules used were those identified as having the best potential for blending with diesel fuel by the DOE Oxygenate Analysis Project [2,3]. The first oxygenated fuel (denoted BM88) contains the oxygenate DBM; the second (denoted GE80) contains the oxygenate TPGME. Compositional information for the test fuels is provided in Table 2, and the oxygenate molecular structures are shown in Figure 3.



Figure 1. Sandia/Caterpillar Optical Research Engine (SCORE) Laboratory in operation.

Table 2. Test Fuel Compositions

Fuel	Composition (by volume)	Oxygen Content (by weight)
CN80	76.5% C ₁₆ H ₃₄ as NHD ^a 23.5% C ₁₆ H ₃₄ as HMN ^b	0%
BM88	88.0% DBM ^c 7.0% C ₁₆ H ₃₄ as NHD ^a 5.0% EHN ^d	26.5%
GE80	80.0% TPGME ^e 20.0% C ₁₆ H ₃₄ as HMN ^b	25.8%

^a *n*-hexadecane

^b 2,2,4,4,6,8,8-heptamethylnonane

^c di-butyl maleate

^d 2-ethylhexyl nitrate

^e tri-propylene glycol methyl ether

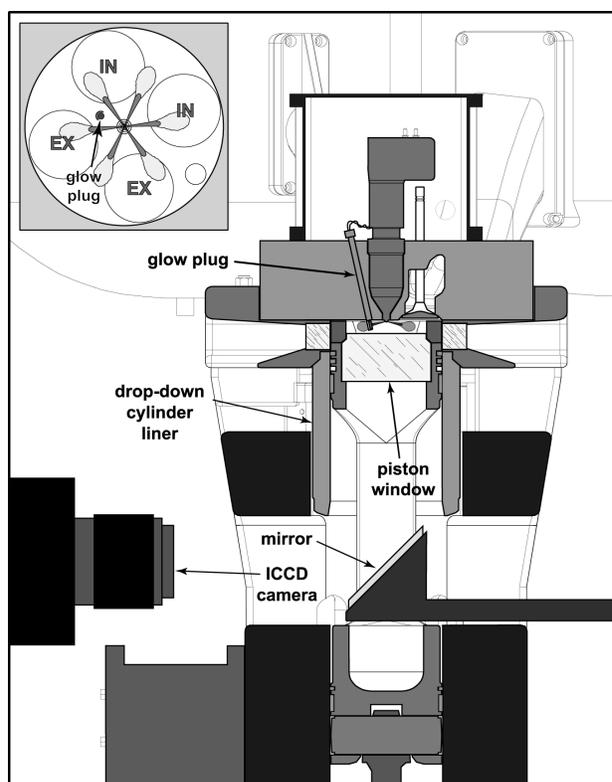


Figure 2. Schematic diagram of the SCORE. Inset: View of combustion chamber showing orientation of fuel sprays with respect to glow plug (note glow plug not energized during these experiments).

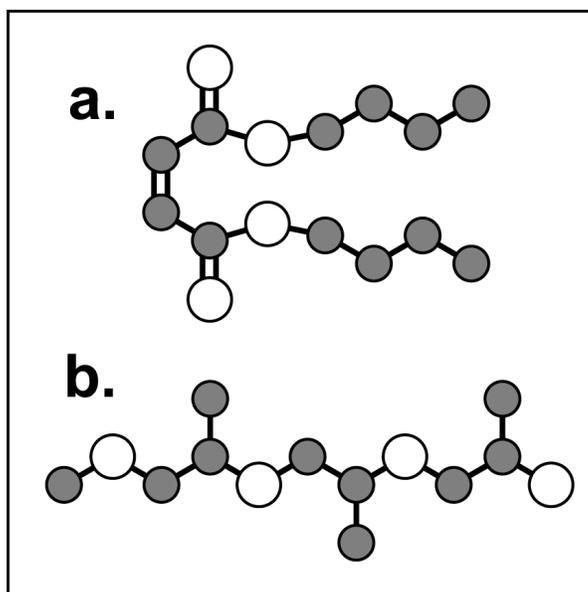


Figure 3. Molecular structures of oxygenate molecules. Dark and light circles represent carbon and oxygen atoms, respectively. Hydrogen atoms omitted for clarity. a. Di-butyl maleate (DBM). b. Tri-propylene glycol methyl ether (TPGME).

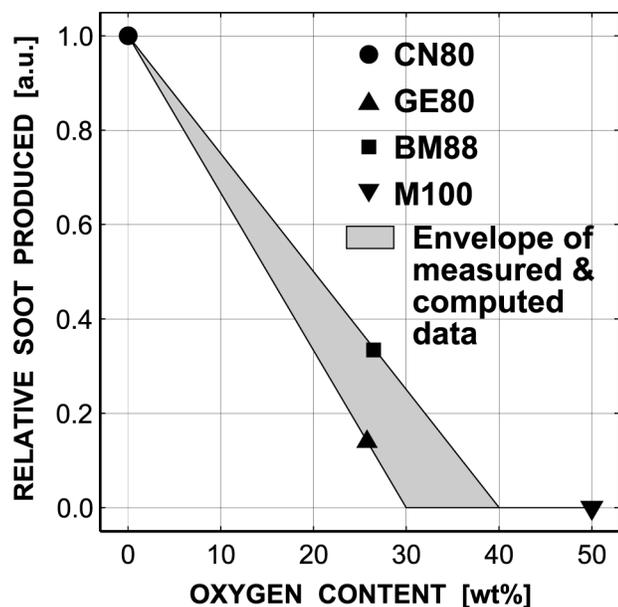


Figure 4. Variation of spatially integrated natural luminosity (SINL) for the test fuels as a function of fuel oxygen content.

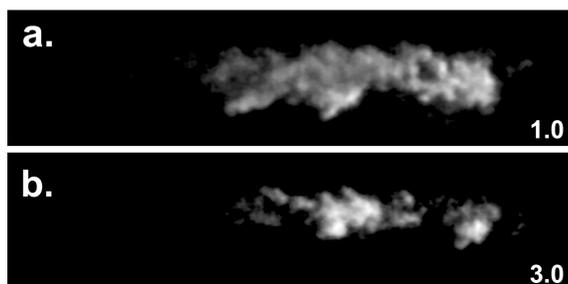


Figure 5. Laser-induced incandescence (LII) images for a. BM88 and b. GE80 fuels. Injector orifice located at center of left edge of image. Width of imaged region is 95 mm. Camera gain provided in lower-right corner of image (lower gain = larger

Results and Conclusions

Previous research conducted in the SCORE laboratory suggested that overall oxygen content is not the only important parameter governing the soot-reduction performance of an oxygenated fuel. Research conducted this year has extended our understanding by establishing that oxygenate molecular structure can play a very important role in soot reduction, especially for highly oxygenated fuels.

One of this year's first tasks was to conduct a detailed mathematical and physical analysis to determine the validity of using SINL as a means to estimate in-cylinder soot concentrations. The analysis showed that comparing peak SINL values provides a conservative method for estimating the soot-reduction potential of the test fuels under the present operating conditions [4]. Figure 4 shows peak SINL values achieved during combustion of the test fuels in this work [4], along with a data point for neat methanol (M100) from Reference [1]. It is evident that the relative amount of soot produced decreases as the oxygen content of the fuel increases. The shaded region in Figure 4 delineates an envelope of results from other studies that have shown that computed soot precursor concentrations and engine-out smoke emissions go to zero when the oxygen content in the fuel reaches 30-40% [5,6]. Note that the data points for BM88 and GE80 are at the high and low ends of this region, respectively, suggesting that TPGME is considerably more effective at reducing soot than DBM.

Figure 5 shows LII images that were acquired in the constant-volume Diesel Combustion simulation Facility (DCSF) at conditions matched to those in the optical engine. They yield the same trend as the SINL results, namely that BM88 produces significantly more in-cylinder soot than GE80.

Why would one oxygenated fuel be more effective at reducing soot than another, even when their oxygen content, combustion phasing, adiabatic flame temperature, and all engine operating conditions are matched? Two possible explanations are differences in air entrainment and differences in molecular-structure/chemical characteristics of the fuels.

One important parameter affecting air entrainment is the distance a diesel flame stands off from the injector orifice, i.e., the lift-off length [7]. The longer the lift-off length, the more air can be mixed into the fuel-rich core of the diesel spray before combustion begins, and the less soot is produced. Figure 6 shows flame lift-off lengths measured for the two oxygenated fuels in the DCSF. While the lift-off lengths are slightly different, analysis has shown that this factor alone cannot

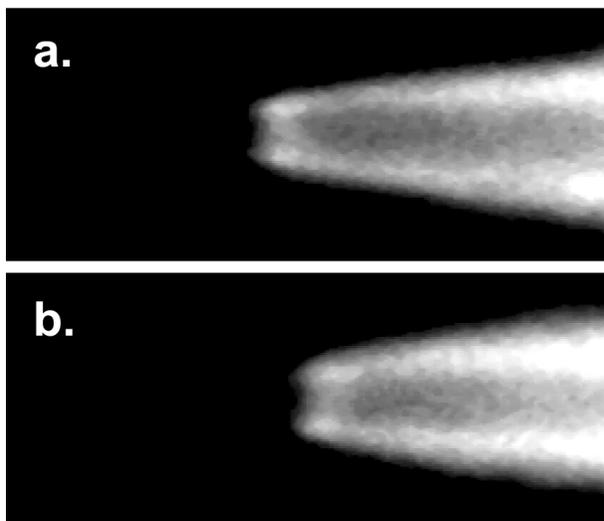


Figure 6. Lift-off length images for a. BM88 and b. GE80 fuels. Injector orifice located at center of left edge of image. Width of imaged region is 40 mm. Difference in lift-off length is not sufficient to account for difference in amount of soot produced.

account for the large disparity between in-cylinder soot concentrations.

It is not surprising that molecular-structure/chemical effects could cause the observed difference in soot between the two oxygenated fuels. After all, great effort was expended to vary only the type of oxygenate molecule in the experiments. One chemical effect was discovered by conducting a double-distillation analysis of DBM, which showed evidence of 5-10% polymerization and thermal decomposition before complete vaporization. This phenomenon was not observed for either of the other test fuels. It could lead to increased soot production as well as deposit formation in injector tips, and may preclude further consideration of DBM as a viable diesel oxygenate. Furthermore, chemical-kinetic analyses indicate that DBM is more likely to produce soot precursors during oxidation than TPGME [8]. Experiments using AMS diagnostics are currently underway in the SCORE laboratory to test this hypothesis [9] and to identify improved oxygenate molecules.

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FY 2002 Award

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B. Chemical Characterization of Toxicologically Relevant Compounds from Diesel Emissions: A Project of the Fuels/Particulate Matter Initiative; Phase I & II

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This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

E. Toxic Emissions

Tasks

2. Fuel & Lubricant Properties - Engine-Out Emissions

Objectives

- Investigate the role of fuels on tailpipe exhaust emissions of potentially toxicologically relevant compounds, utilizing a diesel oxidation catalyst and a catalyzed particulate filter.
- Investigate low-NO_x engine operation effects on diesel exhaust emission toxicity.
- Investigate role of high molecular weight oxygenate on diesel exhaust toxicity.
- Determine polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of exhaust particulate matter, gaseous exhaust PAH, and other gaseous exhaust "toxics" collected from a diesel engine using various fuel compositions.

Approach

- A Daimler-Benz OM611 diesel engine was used to determine the effect of diesel fuel type on toxicologically relevant compounds from engine-out exhaust emissions.
- Engine was controlled by SwRI Rapid Prototyping Electronic Control System (RPECS).
- Test matrix to include seven fuels, including two oxygenate blends with tripropylene glycol monomethyl ether (TPGME) and one oxygenate blend with dibutyl maleate (DBM), operated over four speed/load points.
- Engine to be operated utilizing pilot fuel injection at a low-NO_x engine-out calibration specific for each fuel and speed/load point.
- Measurements to be taken at engine-out, after the diesel oxidation catalyst, and after the catalyzed particulate filter.

Accomplishments

- Project plan was fully coordinated with DOE and industry. Industry defined NO_x emission index targets.
- Industry was consulted to define a methodology to achieve low engine-out NO_x emission index target.

- Engine-out NO_x emission index reduction of 45% is achievable from stock engine modal calibrations.

Future Directions

- Determine fuel effects on emission characterization utilizing a NO_x trap.
- Determine fuel effects on emission characterization with NO_x and particulate trap regeneration.
- Determine fuel effects on emission characterization for premixed charge compression ignition combustion.

Introduction

The Particulate Matter (PM) Analysis Phase II project is part of an overall study that examines the effect of oxygenated compounds in diesel fuel on the emissions of particulate matter, oxides of nitrogen, and fuel economy when emission control devices are used. The project will focus on the chemical characterization of emissions of compounds with known or suspected toxicological properties. Exhaust emissions of these compounds will be measured before and after emission control devices to better understand the effects of emission control devices and alternative fuels.

Objective

The control of NO_x emissions is probably the greatest technical challenge in meeting future emission regulations for diesel engines. In this project, lowering engine-out emissions of NO_x by increasing exhaust gas recirculation (EGR) and retarding timing will likely cause an increase in PM emissions. In Phase I of this project, it was shown that the use of an oxygenated diesel fuel additive will lower PM emissions. Use of an oxygenated diesel fuel additive thereby can minimize the increase in PM emissions that accompany the techniques used to decrease NO_x emissions.

The overall objective of this project is to better understand the role of fuels and emission control devices on the exhaust emissions of a subset of potentially toxicologically relevant compounds with an engine operated to minimize NO_x emissions. The three objectives of this project are to measure the following pollutants collected from diesel engines under a matrix of engine and fuel conditions:

- Polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of particulate matter
- Gas phase polycyclic aromatic hydrocarbons
- Gaseous toxic compounds (formaldehyde, acetaldehyde, benzene and 1,3-butadiene)

These measurements will be made on engine-out exhaust emissions, and after an oxidation catalyst and a diesel particulate filter.

Approach and Results

PM Analysis II Emission Control System Selection

Discussions were held with Manufacturers of Emission Controls Association (MECA) to specify component configurations for the diesel oxidation catalyst and the diesel particulate filter. The component configurations that were selected are a 1.5L diesel oxidation catalyst and a 2.5L catalyzed wall flow particulate filter. The soot loading capacity of the particulate filter is a nominal 17 grams. It was mentioned that the catalyst “wake-up” temperature range, 170°C-200°C, may be of significant interest for typical light-duty diesel operation. Exploratory engine operation at 1250 and 1500-rpm (1.0 bar- bar-brake mean effective pressure [bmep]) were evaluated to obtain exhaust stack temperatures; at the original equipment manufacturer (OEM) calibration condition, exhaust stack temperature was around 167°C at 1250 rpm, and around 179°C at 1500 rpm. Exploratory runs at a Low-NO_x operating condition with increased EGR and retarded timing increased the exhaust stack temperature at 1500-rpm (1.0 bmep) to 195°C. The Ad Hoc CIDI fuels working group agreed that a mode at the catalyst “wake-up” temperature, defined as Mode 22, 1500-rpm (1.0 bar-bmep), would be used in the test project.

The MECA supplier for the emission control devices coated, canned, baked, and delivered the devices to SwRI. The MECA supplier baked the aftertreatment devices in a 600°C oven for 48 hours prior to delivery. The baking was performed to degas the insulation, packing, and washcoat. The baking will reduce the time required to degreen the devices on the engine. A 1.5L diesel oxidation catalyst (DOC) and a 2.5L catalyzed diesel particulate filter (DPF) were received and installed in the OM611 engine test cell.

The OM611 engine was operated with both emission control devices (ECDs) present to determine the effect of the ECDs on backpressure and engine control. The engine-out backpressure was higher with the ECDs installed; however, control of the engine and EGR stability was not affected.

Efforts were extended to develop a regeneration protocol with the DPF. The regeneration target was to obtain 550°C at the DPF inlet, while operating the engine at Mode 6, 2300-rpm/4.2-bar bmep. The typical exhaust stack temperature for Mode 6 is 395°C. During regeneration, the injection pulse was modified such that the pilot duration was extended to inject ~70% of the fuel with location of the peak pressure of combustion at 7° at top dead center (ATDC). The remaining fuel was injected late cycle, at ~45°ATDC. The DOC converts the late cycle injected hydrocarbons into heat for the DPF. The regeneration to a consistent 115 kilopascal (kPa)-absolute backpressure from a fully loaded DPF takes 90 minutes to complete. It appears the DOC is consuming >90% of the unburned hydrocarbons and oxygen, thus resulting in the slow regeneration of the DPF. However, the strategy was to regenerate the DPF at a condition that would not jeopardize the cylinder pressure transducers installed in the engine. Efforts are being made to alter the regeneration strategy to shorten the burn-off time. The base soot pack appears to be consistent, as determined by DPF weight, at the 115 kPa-absolute backpressure. Six regeneration cycles to 115 kPa-absolute backpressure revealed a spread of 3 grams between the maximum and minimum DPF weight recorded.

Low-NO_x Operating Point Definition

The overall project goal is to define reasonable (not fully optimized) low-NO_x operating conditions.

Substantial reductions in nitrogen oxide index (NO_xEI) are achieved by moving from the conditions of Phase I of this project to the stock OEM calibrations for the engine. Additional NO_xEI reductions are obtained by varying the EGR rate and injection timing. The objective of this effort is to determine the operating points (e.g., injection timing and % EGR) to be used for each of the four modes in the PM Analysis Project-Phase II. For each mode, an attempt to determine the limit between stable and unstable engine operation for Low-NO_x operating conditions was made. New fuel injectors and a fuel injection pump were installed in the OM 611 test engine.

An initial methodology for determining the operating condition parameters was conducted with ECD-1 fuel at the Mode 11 (1500-rpm/2.62-bar bmep) operating condition. The approach was to start at the electronic control module point and add EGR and retard timing, then evaluate NO_x reduction and fuel consumption increase. Initial data suggested EGR is more cost effective for NO_x reduction in terms of fuel consumption, but leads to high smoke levels. Subsequently data sets have been generated for Mode 10 (2000-rpm/2.0-bar bmep), Mode 6 (2300-rpm/4.2 bar-bmep), and Mode 22 (1500-rpm/1.0 bar-bmep). Auto company participants were asked to obtain review/input from their driveability/calibration staff on the EGR and timing sweeps.

The following summary was given for what type of vehicle operation each engine mode represents:

Mode 22: Catalyst Transition Temperature

Mode 11: Low speed cruise

Mode 10: Low speed cruise with slight acceleration

Mode 6: Moderate acceleration

The general rules for selecting Low-NO_x operating conditions were revised based on driveability and other considerations, and are shown in Table 1. The operating condition, which gave the largest NO_x decrease while meeting the tabulated rules, was selected for the specific operating condition.

Table 1. Rules for Defining Low-NO_x Operating Conditions

MODE	EGR	BSFC	BOOST	SMOKE	HC
6	>OEM (16%)	3% maximum increase	50% maximum decrease	100% maximum increase	No rule
10	>OEM (33%)	3% maximum increase	50% maximum decrease	100% maximum increase	No rule
11	>OEM (35%)	3% maximum increase	>0	100% maximum increase	No rule
22	>OEM (51%)	3% maximum increase	N/A	100% maximum increase	100% maximum increase

The Low-NO_x operating points and PM results for all fuels have been generated. Figure 1 shows the OEM and Low-NO_x combustion timing and EGR windows for each test fuel. The box around the Low-NO_x points indicates the combustion timing and EGR tolerances outlined by the Ad Hoc CIDI working group. From Figure 1 it can be noted that all fuels fell within the tolerance box for the Low-NO_x operating condition. Manifold pressure constraints limited EGR levels, and fuel economy impacts limited combustion timing retard for NO_x reduction.

Relative weighted emission index values were calculated for the test fuels, with the ECD-1 fuel used as the base. The relative NO_x versus PM index trade-off is shown in Figure 2. Included in Figure 2 are data for the OEM and Low-NO_x operating conditions, with the results normalized to ECD-1 fuel at the OEM condition. Also included in Figure 2 are estimates of the 95% confidence intervals for the normalized data.

Based on the confidence intervals shown in Figure 2, the OEM operating condition NO_x index of the ECD-1 and Diesel Emission Control-Sulfur Effects (DECSE) fuels are similar to all fuels except Neat Fischer-Tropsch fuel (FT100). FT100 is different from the BP15 and the BP15 based oxygenated fuels. The BP15 and BP15 based oxygenated fuels show a greater NO_x index than ECD-1+TPGME at the OEM operating condition. The relative PM index results at the OEM operating condition suggest FT100 and the oxygenated fuels are similar. The ECD-1, BP15, and the DECSE fuels have higher PM indices than the other fuels, although

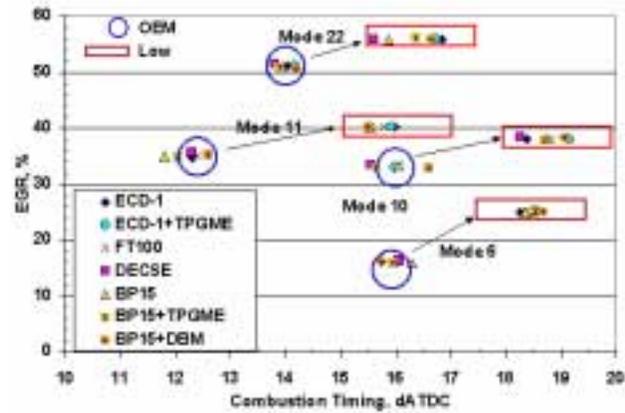


Figure 1. Modal EGR and Combustion Timing Windows for All Fuels

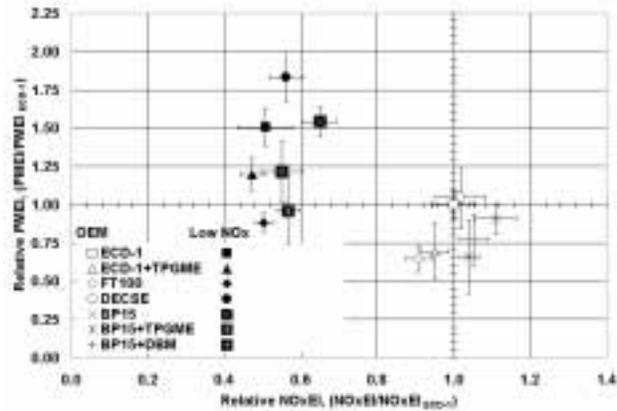


Figure 2. Relative PM and NO_x Emission Indices Trade Off for Test Fuels

the variability suggests this result is not significant. The BP15 fuel has higher PM response than the BP15-based oxygenated fuels for the OEM operating condition.

At the Low-NO_x operating conditions, with the exception of the BP15 fuel, the fuels appear similar in regards to the relative NO_x index. The PM index results at the Low-NO_x condition spread apart, with the PM index from FT100 being lower than any other fuel, yet similar to the BP15+TPGME fuel. The PM index for ECD-1+TPGME is lower than the DECSE and BP15 fuels. Although the ECD-1+TPGME PM index is numerically lower than the ECD-1 fuel, the variability of the weighted result suggests they are

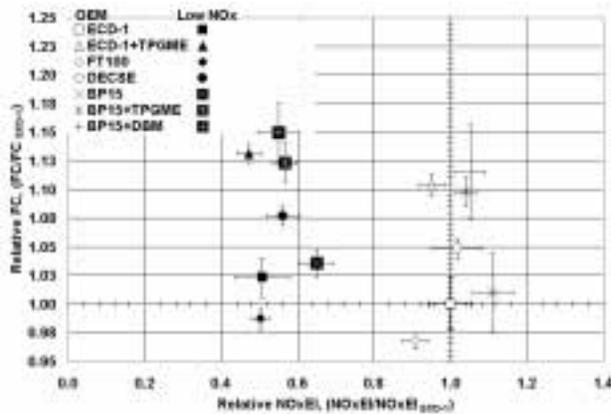


Figure 3. Relative Fuel Consumption Trade Off with NO_x Indices for Test Fuels

similar. The PM index for the BP15+DBM oxygenated fuel is similar to the ECD-1, ECD-1+TPGME, and BP15 fuels. The BP15+TPGME fuel is lower than the other oxygenated fuels for PM index at the Low- NO_x operating condition, and only greater than FT100.

Conclusions

Overall, all fuels are statistically different for relative NO_x index between the OEM and Low- NO_x operating conditions. In general, the relative PM indices are higher at the Low- NO_x condition than the OEM condition.

Relative weighted fuel consumption was calculated and plotted with respect to relative NO_x index in Figure 3 for the OEM and Low- NO_x operating conditions. Overall, the fuel consumption penalty for the Low- NO_x operating conditions is on the order of 2.5 to 3 percent.

Investigation of the role of fuels on tailpipe exhaust emissions of potentially toxicologically relevant compounds, utilizing a diesel oxidation catalyst and a catalyzed particulate filter, will be starting in late FY 2002.

FY 2002 Publication/Presentations

1. D.M. Yost and E.A. Frame, "Particulate Matter Analysis from an Advanced Diesel Engine; Phase I & II", CIDI Engine Combustion, Emission Control, and Fuels R & D, Merit Review and Peer Evaluation, Argonne National Laboratory, 6-8 June 2002.
2. Yost, et. al., "Impact of Engine Operating Conditions on Low- NO_x Emissions in a Light-Duty CIDI Engine using Advanced Fuels," SAE 2002-01-2884.

C. Ultra-low Sulfur Reduction Emission Control Device/Development of an On-board Fuel Sulfur Trap

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Main Subcontractors: Honeywell Consumer Products Group Perrysburg, Ohio, Mack Trucks Hagerstown, Maryland, Marathon (MAP), Findlay, Ohio, Johnson Matthey, West Deptford, New Jersey, American Waste Industries, Maywood, Illinois

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

D. Sulfur Impacts

Tasks

3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions

Objective

- To develop and demonstrate proof-of-concept for an "on-vehicle" desulfurization fuel filter for heavy- and light-duty diesel engines

Approach

- Phase I: Develop a conceptual design and resolve technical barriers concerning removal of sulfur-containing species in low sulfur fuels
- Phase II: Implement high through-put screening techniques for chemistry selection and dynamic testing
- Phase III: Prototype design and testing: adapt research concept into a practical filter module and test its efficacy, produce prototype(s)
- Phase IV: Life cycle studies: study life cycle and regeneration options for spent filters
- Phase V: Validation Testing: engine testing with nitrogen oxides (NO_x) adsorber and test prototype filter on a heavy-duty diesel engine for efficacy, and system performance, and component integration

Accomplishments

- Obtained representative low-sulfur diesel fuels obtained to meet the Environmental Protection Agency (EPA) Tier II standards
- Completed analytical procedures for total sulfur and speciation completed

Future Directions

- Complete conceptual design and initiate analysis and testing
-

Introduction

The goal of this project is to develop an emission control device that can enable engine manufacturers to comply with the EPA emission standards including EPA Tier II Bin 5 for light-duty engines and the new '2007-Rule' for heavy-duty engines. The '2007' rule includes a new diesel fuel sulfur limit that has a maximum of 15 parts per million. Successful integration of the sulfur-removal component into a heavy-duty compressed ignition direct injection (CIDI) vehicle coupled with a post-combustion NO_x adsorber catalyst device will by default be applicable to light-duty CIDI engines. An onboard fuel sulfur removal device can expedite NO_x adsorber technologies by assuring consistently low sulfur content and providing protection from misfueling and out-of-specification fuels. This should be accomplished at relatively modest cost to the end-user because the sulfur-removal device will be an add-on to the existing fuel system, and will be packaged in a conventional engineering format. It is anticipated the cost of the proposed sulfur-removal device to the consumer will represent no more than a low multiple of the current cost of a standard fuel filter.

Approach

The main objective of this project is to demonstrate at the pilot scale level proof-of-concept for a fuel desulfurization filter that is able to reduce sulfur levels in the fuel to tolerable levels which enable the implementation of post-combustion NO_x adsorber technology. The technology developed will rely on Honeywell's expertise in reactive filtration technology. The targeted design and performance of this filter will be developed based on criteria supplied by Johnson Matthey (the NO_x catalyst manufacturer) and Mack Trucks (the CIDI engine manufacturer).

Development incorporates the following key elements: 1) survey of all applicable current and proposed approaches, 2) technical evaluation of potential technologies, 3) laboratory screening of

down-selected approaches, 4) packaging of selected technologies for on-board configuration, 5) prototype design and preparation, 6) pilot scale life-testing and efficacy testing of the filter, and, 7) development of approaches to recycle/regenerate the spent filters.

Results

This project began in April 2002. Representative fuel samples have been prepared and sufficient quantities of these are now in place to begin the experimental stage of the project. The analytical procedures are also now in place for measuring total sulfur and speciation of the sulfur contaminants.

D. C1 Chemistry for Production of Clean Liquid Transportation Fuels and Hydrogen

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Main Subcontractors: West Virginia University, Morgantown, West Virginia, University of Pittsburgh, Pittsburgh, Pennsylvania, University of Utah, Salt Lake City, Utah, Auburn University, Auburn, Alabama

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

G. Advanced Fuel Production and Cost

Tasks

5. Refinery and Fuel Processing Economics

Objectives

- C1 chemistry refers to reaction processes that use feedstocks that consist of molecules containing one carbon atom [synthesis gas (a mixture of CO and H₂), methane (CH₄), carbon dioxide (CO₂), carbon monoxide (CO), and methanol (CH₃OH)]. The major objectives of this project are to develop C1 technology for the production of ultra-clean, high efficiency, liquid transportation fuels and hydrogen.

Approach

- The Consortium for Fossil Fuel Science (CFFS) is a research consortium with participants from five universities - the University of Kentucky, University of Pittsburgh, University of Utah, West Virginia University, and Auburn University. The CFFS universities are collaborating on a research project to develop C1 chemistry processes to produce clean transportation fuel from resources such as coal and natural gas, which are more plentiful domestically than petroleum. The processes under development will convert feedstocks containing one carbon atom per molecular unit into ultra clean liquid transportation fuels (gasoline, diesel, and jet fuel) and hydrogen. The feedstocks include syngas, a mixture of carbon monoxide and hydrogen produced by coal gasification or reforming of natural gas, methane, methanol, carbon dioxide, and carbon monoxide. An Industrial Advisory Board with representatives from Chevron, Eastman Chemical, Energy International, the Department of Defense, Conoco, and Tier Associates provides guidance on the practicality of the research.

Accomplishments

- Small additions of compounds with carbon-carbon triple bonds to the Fischer-Tropsch synthesis have been shown to improve the products by increasing their oxygenate content.

- Operation of Fischer-Tropsch synthesis under supercritical fluid (SCF) solvent conditions increases CO conversion, decreases the yield of C₁-C₃ gases, and increases C₇-C₂₄ 1-olefin yield.
- New platinum/tungsten/zirconium dioxide (Pt/W/ZrO₂) catalysts have been developed that are very effective at cracking Fischer-Tropsch wax into diesel fuel.
- Nanoscale, binary, iron-based catalysts containing molybdenum (Mo), palladium (Pd), or nickel (Ni) are very active for the decomposition of methane and ethane, producing pure hydrogen and carbon nanotubes. The nanotubes derived from ethane exhibit an interesting stacked traffic cone structure.
- A small diesel engine test facility has been established and used to demonstrate the beneficial effects of oxygenate additives in reducing particulate matter (PM) emissions.

Future directions

- The CFFS will continue to work on further improvement in the Fischer-Tropsch synthesis and on developments of innovative approaches for producing pure hydrogen.

Introduction

The CFFS C1 chemistry research program has produced a number of significant research achievements in its first three years. In this report, a brief summary is given of some of these achievements, with emphasis on Fischer-Tropsch synthesis of fuels and hydrogen.

Approach and Results

Novel Approaches to Fischer-Tropsch Synthesis

Fischer-Tropsch synthesis is the best-known C1 chemistry process for producing transportation fuel from syngas. CFFS research has produced a number of innovations on the Fischer-Tropsch process. In research conducted at the University of Pittsburgh, it has been discovered that small (~1%) additions of probe molecules with carbon-carbon triple bonds dramatically enhance the presence of oxygenated products. This significantly decreases emissions of PM, which is a critical issue for diesel and jet fuels. Using 1-hexyne as the probe molecule additive, much higher yields of Fischer-Tropsch products in the C₆ to C₂₀ range were obtained. Gas chromatography-mass spectroscopy analysis detected such oxygenated species as 1-heptanal, 2-heptanal, 1 heptanol, 1-octanol, 1-undecanol, and 1-tetradecanol.

Other work at the University of Pittsburgh has focused on catalytic hydrocracking of Fischer-Tropsch wax, which is typically 65-75% of the

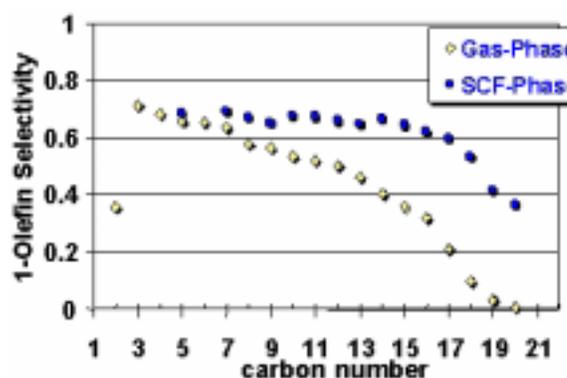


Figure 1. The yield of 1-olefins from FT synthesis is markedly increased under SCF conditions.

Fischer-Tropsch product. Pt/W/ZrO₂ catalysts have been developed that are very effective at converting Fischer-Tropsch wax into a product that is approximately 70% diesel fuel, 25% gasoline, and 5% lube oil.^(1,2)

Fischer-Tropsch synthesis in supercritical fluid (SCF) solvents is under investigation at Auburn University. The SCF media has the advantage of gas-like diffusivities and liquid-like solubilities and heat transfer properties. In experiments using SCF hexane and a commercial cobalt Fischer-Tropsch catalyst, total syngas conversion was increased over the gas-phase reaction from approximately 50% to 80%, and selectivity to heavier products and olefins was increased.^(3,4) The yield of C₁-C₃ gases was decreased by approximately 40% in the SCF reaction, while the C₇-C₂₄ 1-olefin yield was

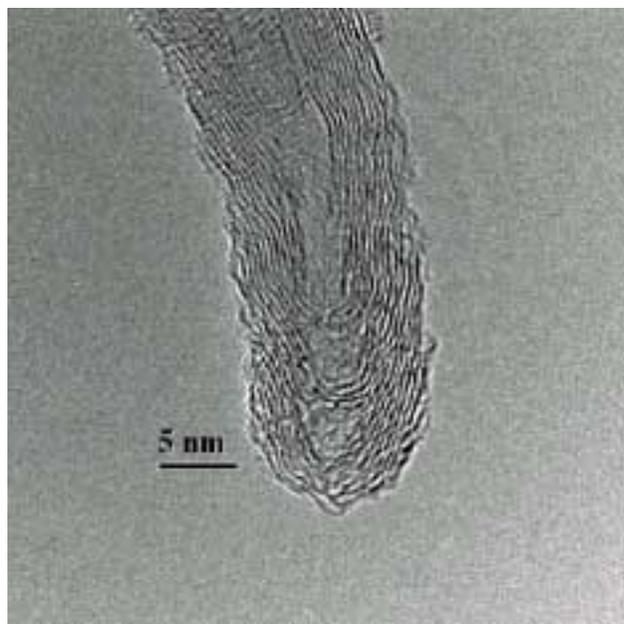


Figure 2. Carbon nanotubes formed by decomposition of ethane at 500°C exhibit an interesting nested traffic cone structure.

markedly increased (Figure 1). Future research will focus on other SCF solvents (propane, pentane, carbon dioxide, and mixtures), novel catalyst designs, and pressure tuning to alter product selectivity and yield.

Hydrogen

Traditionally, hydrogen has been produced by partial oxidation of methane or gasification of coal to produce synthesis gas, followed by the water-gas shift reaction to convert CO to CO₂ and produce more hydrogen. To achieve the purity required by polymer-electrolyte proton exchange membrane fuel cells (<10 ppm CO), further purification (reverse methanation or catalytic oxidation of CO) and separation procedures are required. Research at the University of Kentucky is focused on producing pure hydrogen in a single step by catalytic dehydrogenation of hydrocarbons. Nanoscale, binary Fe-based catalysts containing Mo, Pd or Ni and supported on high surface area alumina have been developed that are very effective for the non-oxidative catalytic decomposition of methane into pure hydrogen and carbon nanotubes.⁽¹⁾ The key factor influencing catalyst activity is the efficient

removal of carbon from the catalyst surface in the form of multi-walled nanotubes, a valuable by-product with potential applications in electronics, high strength materials, and hydrogen storage. More recent experiments on the catalytic dehydrogenation of ethane have also produced promising results.⁽²⁾ Yields of 80-90% of pure hydrogen have been obtained from both methane and ethane at relatively low temperatures of 700-800°C. The nanotube structure produced by ethane exhibits an interesting stacked traffic cone structure at low decomposition temperatures (500°C, Figure 2). Such open nanotube structures appear promising for hydrogen storage. This is being investigated in collaboration with Dr. Brad Bockrath, a scientist at the U.S. Department of Energy National Energy Technology Laboratory.

Future research will be focused on catalytic dehydrogenation of liquid hydrocarbons, a critical problem for fuel cell-powered vehicles, and on development of a continuous process for catalytic production of pure hydrogen and carbon nanotubes from light alkanes.

Conclusions

Small additions (1%) of compounds with carbon-carbon triple bonds to the Fischer-Tropsch synthesis improve the product fuels by increasing their oxygenate content.

Operation of Fischer-Tropsch synthesis under SCF solvent conditions increases both the yield and olefin content of the products.

Pure hydrogen and carbon nanotubes, a valuable byproduct, are readily produced by catalytic decomposition of methane or ethane using nanoscale, binary, iron-based catalysts containing molybdenum, palladium, or nickel and supported on alumina.

New Pt/W/ZrO₂ catalysts have been developed that are very effective at cracking Fischer-Tropsch wax into diesel fuel.

Other Results of Interest

Interesting results from several additional C1 research projects are briefly summarized below.

- C1 processes for producing ethylene and propylene from methanol are being

developed at Auburn University. These processes use novel silica-aluminophosphate catalysts.

- Catalytic C1 processes have been developed at West Virginia University, Auburn University, and the University of Utah to produce organic carbonates, higher ethers, and higher alcohols for use as additives to diesel fuel or gasoline. Tests conducted using a small diesel engine test facility recently established at the University of Utah have established that such additives significantly decrease particulate matter emissions.
- Binary transition metal carbide catalysts developed at West Virginia University are found to have excellent activities and lifetimes for reforming of methane using carbon dioxide.

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VI. MODELING/DATA ANALYSIS/ASSESSMENTS

A. The Impact of Oxygenated Blending Compounds on PM and NO_x Formation of Diesel Fuel Blends

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This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

B. PM Emissions

Tasks

5e. R&D on PM Reducing Technologies

Objectives

- Characterize the role of oxygenated additives in reduction of particulate matter (PM) emissions from diesel engines
- Develop detailed chemical kinetics reaction models for oxygenated hydrocarbon fuel additives
- Compare soot reduction potential of different oxygenated additives

Approach

- Identify potential diesel additives and their molecular structures
- Develop kinetic reaction mechanisms for the oxygenated additives
- Compute the ignition of each fuel mixture or model the flame structures for the fuel and additive mixtures
- Compare predicted levels of PM and NO_x with and without additives and use a detailed chemical models to determine the mechanisms for the changes

Accomplishments

- Predicted reductions in PM emissions for mixtures of diesel fuel with addition of biodiesel fuels, dibutyl maleate and tripropylene glycol monomethyl ether
- Established that newly proposed oxygenated additives suppressed PM production at approximately the same rate as previous additives studied
- Based on kinetic model predictions, determined limits of validity of existing correlation between amount of oxygen in diesel/additive fuel mixture and PM reduction that agreed with experimental results in diesel engines

Future Directions

- Extend model capabilities to additional oxygenated blending compounds
- Increase collaborations with projects outside Lawrence Livermore National Laboratory (LLNL) dealing with diesel fuel issues

Introduction

Experimental diesel engine studies have indicated that when oxygen is added to diesel fuel, soot production in the engine is reduced. The soot reduction appears to be largely independent of the way oxygen is incorporated into the reactants, including entrainment of additional air into the reacting gases or direct inclusion of oxygen atoms into the diesel fuel molecules.

The present study examines possible diesel fuels which have incorporated oxygen atoms into the molecular structure of the fuel itself. Following past studies of oxygenated diesel fuels such as methanol, dimethyl ether, and dimethoxy methane, this work studies oxygenated fuels which have been selected by industry consultants on the basis of potential for improving performance in diesel engines.

Approach

Chemical kinetic modeling has been developed uniquely at LLNL to investigate combustion of hydrocarbon fuels in practical combustion systems such as diesel engines. The basic approach is to integrate chemical rate equations for chemical systems of interest, within boundary conditions related to the specific system of importance. This approach has been used extensively [1-4] for diesel engine combustion, providing understanding of ignition, soot production, and NO_x emissions from diesel engines in fundamental chemical terms.

The underlying concept is that diesel ignition takes place at very fuel-rich conditions, producing a mixture of chemical species concentrations that are high in those species such as acetylene, ethene, propene and others which are well known to lead to soot production. Some changes in combustion conditions reduce the post-ignition levels of these soot precursors and reduce soot production, while other changes lead to increased soot emissions. The

LLNL project computes this rich ignition using kinetic modeling, leading to predictions of the effect such changes might have on soot production and emissions.

Kinetic reaction models were developed for the oxygenated additives proposed by a DOE/industry panel of experts. We then computed diesel ignition and combustion using heptane [5] as a reasonable diesel fuel surrogate model, mixed with oxygenated additives. The impact of the additive on predicted levels of soot-producing chemical species was then assessed.

Results

Using operational insights derived from recent diesel engine experiments by Dec [6], we assumed that soot production in diesel combustion occurs from reactions of chemical species created in fuel-rich ignition near the fuel injection location. Because there is insufficient oxygen in this region to burn the fuel completely, the hydrocarbon species remaining there react instead to produce soot. Our kinetics calculations show that when the fuel itself contains some oxygen, that oxygen helps convert more of the ignition products into chemical species that do not contribute to soot production.

During the past year, the LLNL project has examined two important oxygenated hydrocarbon species that have been proposed as possible diesel fuels. These are dibutyl maleate (DBM) and tripropylene glycol monomethyl ether (TPGME), both of which include significant amounts of oxygen imbedded in the primarily hydrocarbon fuel molecule. Schematic diagrams of the structures of these two species are shown Figure 1. Detailed chemical kinetic reaction mechanisms were developed for both of these fuels, and the resulting models were used to assess their sooting tendencies.

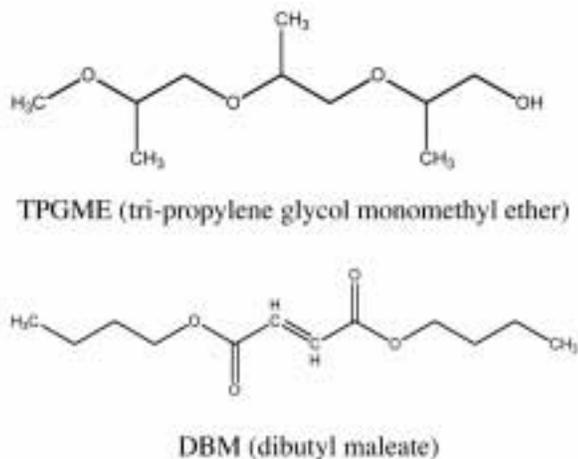


Figure 1. Schematic Chemical Structure Diagrams for Proposed oxygenated Diesel Fuel Components Tripropylene Glycol Monomethyl Ether and Dibutyl Maleate

The model calculations indicate that the distribution of oxygen atoms within the fuel molecule can have a significant influence on the anti-sooting effects of the oxygen atoms. Our work supports a view that oxygen atoms within a fuel molecule form C-O bonds that remove the C atom from the pool of species which can eventually produce soot. Each O atom removes one C atom from the sooting environment, and TPGME is an excellent example of a fuel in which this mechanism can be seen.

However, in DBM, the available oxygen atoms are less well distributed, and in some cases two oxygen atoms produce CO₂ directly from the decomposition of the additive. As a result, the total population of O atoms in the fuel are not as effective at sequestering carbon atoms as in TPGME, so DBM is less effective as a soot reduction fuel additive than TPGME. This analysis is consistent with recent experimental results from Sandia National Laboratories in Livermore. Ongoing kinetic analyses are examining the implications of these results and may lead to new definitions of potentially important diesel fuels for engine combustion. In addition, this work may lead to better analyses of the soot reduction capacities of other alternative diesel fuels. In particular, these kinetic results suggest that biodiesel fuels may have the same reduction in oxygen additive effectiveness as that noted above for

DBM. The methyl ester group in biodiesel fuels has the potential to produce CO₂ directly, making the oxygen content of the biodiesel fuel less able to capture one C atom for every O atom in the fuel and reducing the proportional effectiveness of the fuel-bound oxygen.

Conclusions

Kinetic modeling provides a unique tool to analyze combustion properties of potential alternative fuels for diesel engines. This can provide a way to screen proposed new fuel classes or types that may be important in applied studies. A kinetic model can be very cost-effective as an alternative to experimental analyses, and computations can also provide a fundamental explanation of the reasons for the observed results.

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B. System Emissions Reduction Analysis for Automobiles, Light Trucks, and Heavy-Duty Engines

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Main Subcontractor: Ricardo, Inc., Belleville, Michigan

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

- A. Fuel Property Effects on Engine Emissions and Efficiency
- B. Fuel Property Effects on Exhaust Emission Control System Technology
- D. Sulfur Impacts
- E. Toxic Emissions
- F. Advanced Fuel Production and Cost

Tasks

- 2. Fuel & Lubricant Properties - Engine-Out Emissions
- 3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions
- 4. Develop Empirical Relationships

Objectives

- Establish system emissions reduction (SER) analysis modeling components.
- Develop and use systems level analysis tools that incorporate the empirical emission relationships and first principle models to identify the best pathways for achieving the technical targets for compression ignition direct injection (CIDI) engines, identified in the Advanced Petroleum-Based Fuels (APBF) Multiyear Program Plan.

Approach

- Conduct an analysis comparing the emissions reduction and fuel penalty trade-off of three CIDI emissions control technology bundles for the sport utility vehicle (SUV) analysis platform.
- Develop an array of 1-D engine models to match the APBF activity analysis platforms.
- Augment the Advanced Vehicle Simulator (ADVISOR) with new component data and engine maps developed from the 1-D engine models.

- Recommend future analyses and continue to expand input databases, identify gaps in the data required for accurate predictions, and use this information as a guide to develop future research and development projects.

Accomplishments

- Initiated an analysis comparing the emissions reduction and fuel penalty trade-off for selective catalytic reduction (SCR), nitrogen oxides (NO_x) adsorber, and DeNO_x catalysts all with diesel particulate filters for the SUV platform equipped with a 5.0 liter CIDI engine.
- Developed two of the four planned 1-D engine models using the WAVE software. The 2.2 liter, 5.0 liter, and 7.3 liter models are complete, and the 11.0 liter model is currently under development.
- Used the 7.3 liter WAVE 1-D engine model to demonstrate the process for developing engine emissions and efficiency maps that can be used in ADVISOR.

Future Directions

- Expand component models and refine model integration.
- Analyze pathways for reducing emissions for three platforms and investigate specific applications of analysis tools such as the effect of compression ratio, exhaust gas recirculation (EGR), and aftertreatment devices on efficiency, and fuel formulation effects on emissions.
- Develop a process to validate the model at a systems level.
- Identify and collect relevant data already existing from research partners.

Introduction

The APBF program seeks to identify and establish the ability of advanced petroleum fuels and non-petroleum fuel blending components to enable light-duty CIDI vehicles and heavy-duty CIDI engines to meet future emission standards, while continuing to improve engine efficiency and durability.

A component of the APBF program is establishing a SER analysis framework for automotive, light truck, and heavy-duty engine applications. This framework focuses on applying a systems approach to analyzing emission reduction pathways and fuel options. Establishing the SER analysis approach requires analyzing available data and developing maps and submodels to add to the existing ADVISOR vehicle system model.

Approach

The National Renewable Energy Laboratory (NREL) is using fuel property and emission data from Advanced Petroleum Based Fuels - Diesel Emissions Control (APBF-DEC) and associated

empirical data relationships, in conjunction with first-principle models to evaluate the most promising pathways for reducing emissions using the SER approach. The system concept consists of an analysis tool that accounts for the interaction of fuel, combustion strategy, and aftertreatment. This approach is being built around NREL's ADVISOR (advanced vehicle simulator). ADVISOR requires a detailed map of gaseous emissions, particulate matter (PM) emissions (real-time), fuel consumption, exhaust and EGR temperatures, at many engine speeds and loads. Such maps can be acquired as actual datasets from engine testing or generated using one-dimensional engine models with a more limited (i.e. 10-mode) dataset and various engine parameters as input. This work will involve continually developing these engine performance maps using data acquired from other APBF projects, as well as incorporating conversion efficiency data (as a function of exhaust temperature and flow parameters) for various emission control devices. Empirical relationships of emissions and specific, targeted fuel properties such as sulfur content, cetane number, and aromatic content will be used to estimate the impacts of fuel properties. These

components will be used to evaluate the best pathways for achieving the technical targets of the overall APBF-DEC program.

The SER approach is designed around the following:

- Use ADVISOR as an analysis platform to link system components (i.e. empirical emission relationships, first principle models, and parameterized models). Identify the best pathways for achieving the technical targets on a vehicle level as defined by the APBF program.
- Collect data sets from engine laboratories and develop empirical relationships linking emissions to fuel properties.
- Develop 1-D engine models for vehicle platforms for which complete datasets are not available. Expand the CIDI engine map library in ADVISOR and provide enhanced exhaust gas characteristics to be used as inputs to aftertreatment submodels.
- Expand the emissions control and aftertreatment modeling capabilities in ADVISOR in order to enhance emissions predictions.

Results

Three primary activities contributed to results in FY02. The first was emissions reduction fuel penalty trade-off analysis of three CIDI emissions control technologies for one vehicle analysis pathway. The second was the development of 1-D engine models for each of the analysis platforms using the WAVE software. The third was the development of engine efficiency and emissions maps for ADVISOR using the 1-D engine models.

Emissions Reduction Fuel Penalty Trade-off Analysis

The first phase of this effort was to assess the emissions reduction and fuel economy trade-offs of three emissions control technology bundles that are anticipated to be the best approached to meeting Tier 2 emissions standards for CIDI applications in the near term.

The technologies evaluated included:

- NO_x adsorber catalyst with a catalyzed particulate filter
- SCR with a catalyzed particulate filter
- Lean NO_x catalyst with a catalyzed particulate filter

Each of these emissions control systems will be evaluated for the SUV or light-duty pick-up CIDI (5.0 L) vehicle platforms.

For the purpose of this analysis, it was assumed that the analysis vehicle will be equipped with state-of-the-art engine technology, including charge air cooler, turbocharger, and EGR. In addition, it will be assumed that all systems were used in conjunction with ultra low sulfur fuel (< 15 parts per million).

The emissions reduction estimates and fuel consumption trade-off analysis were developed in two separate formats. The first format reports the fuel consumption relative to achieving the Tier 2 -bin 5 emission levels (0.07 grams per mile [g/mi] NO_x and 0.01 g/mi PM). The fuel consumption change was reported in percent change from a baseline of a current production diesel vehicle for each platform. That is, simulated emissions and fuel consumption baselining was required as part of this effort. The second format reports the fuel consumption and emissions reduction trade off incrementally, as grams of fuel used per gram of emission avoided. Finally, the above information is reported graphically, showing the maximum simulated reduction capabilities of all three, technology bundles and the accompanying fuel consumption increases.

To the highest degree possible, all aspects of the emissions control systems will be accounted for in this analysis. That is, all reductants (fuel or urea) and all electrical or other engine parasitic load requirements are converted into equivalent fuel consumption units. This effort will require the use of a variety of analysis tools including ADVISOR, WAVE and MATLABTM. In some cases it will be necessary to utilize a variety of modeling and analytical tools, as well as empirical information and data from published studies in order to fill in gaps in simulation capabilities.

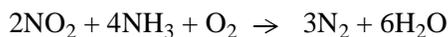
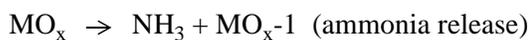
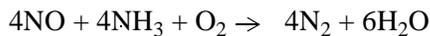
To date, baseline engine-out simulations have been completed, an SUV vehicle model has been developed in ADVISOR, and an SCR model has been developed. Details related to the general emissions control modeling approach and the SCR model follow.

The general framework for all the emissions control technology models is built around MATLAB™ Simulink™. These 1-D, quasi-steady models are designed for an "intermediate level of complexity" and include:

- Mass transfer through the catalyst
- Diffusion of exhaust species to and from the monolith
- Heat transfer between the monolith and the exhaust stream and between the monolith and the ambient
- Global chemical reaction kinetics
- Heat of reaction

The models allow the user to define the number of axial segments into which the catalyst is divided. All simulations for this study will be performed with 20 to 25 segments.

The first of the aftertreatment technologies modeled was the urea-based SCR. For this study, a somewhat simplified model is used. A urea solution is injected into the exhaust upstream from the catalyst, which ideally, given sufficient time and exhaust temperature, decomposes to ammonia. The ammonia then reduces the NO_x to N_2 in the presence of the precious metals of the catalyst. Although sources report many NO_x reduction mechanisms, a five reaction set approach was taken to model the SCR:



More complex reaction sets are difficult to tune, especially given the level of detail of data in

published literature. Likewise, global chemical reaction rate equations are difficult to locate. Therefore, the following rate mechanisms were assumed:

$$R_1 = \frac{A_1 e^{-B_1/T} [\text{NO}] [\text{NH}_3]}{1 + C_1 e^{-D_1/T} [\text{NH}_3]}$$

$$R_2 = A_2 [\text{MO}_{x-1}] [\text{NH}_3]$$

$$R_3 = A_3 [\text{MO}_x] [\text{NH}_3]$$

$$R_4 = \frac{A_4 e^{-B_4/T} [\text{NO}_2] [\text{NH}_3]}{1 + C_4 e^{-D_4/T} [\text{NH}_3]}$$

$$R_5 = \frac{A_5 e^{-B_5/T} [\text{NO}] [\text{NO}_2] [\text{NH}_3]}{1 + C_5 e^{-D_5/T} [\text{NH}_3]}$$

Where:

R = reaction rate (kmol/s)

[x] = mole fraction of species 'x'

T = monolith temperature (K)

To tune the pre-exponential and exponential constants in the rate equations, data from Blakeman, Chandler, John, and Wilkins was used. Catalyst 'B' of this reference exhibits very good performance at low temperatures, especially when sufficient NO_2 is present. Blakeman et al. reports catalyst 'B' results with NO only stream and a 50/50 mix of NO and NO_2 , which allowed tuning of both reactions 1 and 5. Reaction 4 was assumed to have the same constants as Reaction 1. The model achieves a very good match with the data between 150 and 275°C. Since there is no NO_2 in the stream, just NO , this result is solely due to Reaction 1.

Development of 1-D Engine Models

The development of four 1-D engine models using the WAVE software was planned under this task. The primary objective of this was to develop detailed, calibrated WAVE engine models (with supporting data) of the following three diesel engine types, intended to match the SER analysis platforms.

- Automobile class 2.2 liter turbocharged high speed direct injection (HSDI)

- Light-duty truck class turbocharged 7.3 liter
- Light-duty truck class turbocharged scaled 5.0 liter
- Heavy-duty truck class turbocharged 11.0 liter

To date, three of the four models have been developed. These include the 2.2 liter HSDI engine, the Navistar 7.3 liter turbocharged CIDI V8, and the 5.0 liter engine scaled from the 7.3 liter model. Figure 1 shows the WAVE graphical representation of the 2.2 liter HSDI engine.

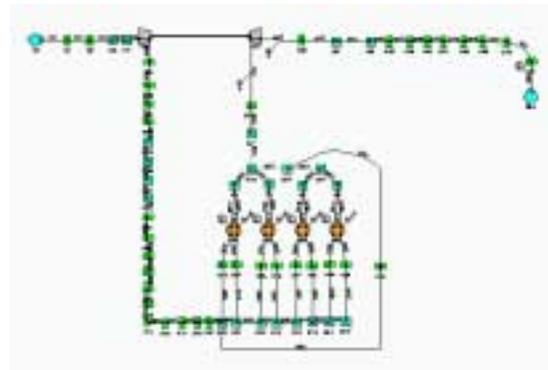


Figure 1. Graphical Representation of the WAVE 2.2 L HSDI Engine Model

Development of ADVISOR Engine Maps from 1-D Engine Models

One of the intended functions of the above models is to use them as a pre-processor for ADVISOR. In this capacity the WAVE model would be used to sweep an array of engine operating points in order to produce efficiency and performance maps that could then be integrated with ADVISOR. The 7.3 liter model was used to produce an engine efficiency map in the MATLAB™ Simulink™ environment so that it could be used by ADVISOR. This process consists of performing a WAVE simulation over ten speed and load points and processing then output into an appropriate matrix format for ADVISOR. Figure 2 shows the engine efficiency map developed from a WAVE simulation for the 7.3 liter Navistar engine. This map can be compared with the efficiency map for this engine based on data from an engine dynamometer over eight steady-state points, shown in Figure 3. The map developed from simulated data match the empirical map reasonably well, with an error range of 2-12 percent depending on the operating point.

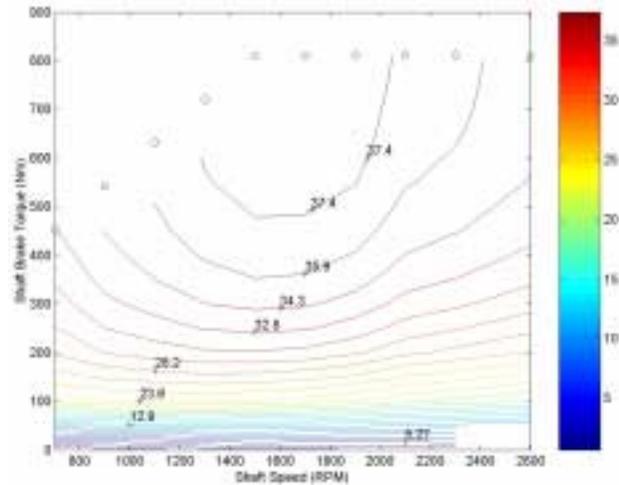


Figure 2. Engine Efficiency Map Developed with WAVE for the 7.3 L Engine

Conclusions

Progress has been made on developing components necessary to enable a system level analysis of the emissions pathways for advanced engines and vehicles. Relationships between fuel and emissions data obtained from testing engines, vehicles, and advanced emission control devices are being developed in submodels that form the building blocks of the SER framework. This framework will provide the capability to predict potential emissions and efficiency improvements for automobiles, light-trucks, and heavy-duty engines.

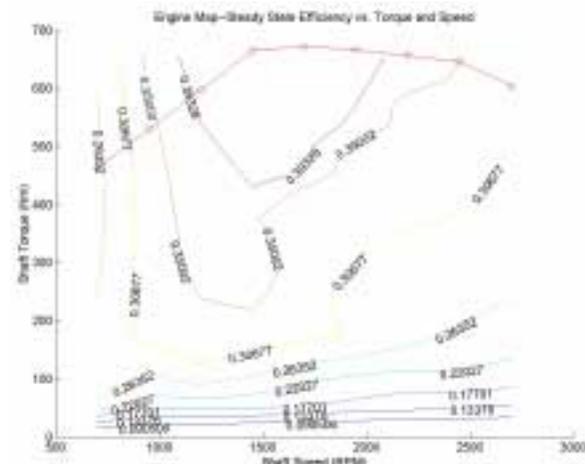


Figure3. Engine Efficiency Map Developed from Dynamometer Data for the 7.3 L Engine

Future efforts will focus on: 1) expanding the number of parameterized aftertreatment submodels, 2) enhancing the empirical data relationships previously developed, and 3) applying the analysis tool. Significant effort will be focused on continuing to develop an integrated systems model.

Additional effort will be devoted to developing fuel property versus emissions correlations using NREL's existing database, enhancing NREL's database, and incorporating other fuel property emissions databases such as the one being developed by the Environmental Protection Agency. The project will continue to focus on evaluating three technology platforms (automobile, light-duty truck, and heavy-duty engine), and will emphasize the inclusion of a heavy-duty engine model into ADVISOR. The project will also evaluate applications related to these platforms as required by DOE and the needs of the APBF-DEC program. The SER project will provide DOE with analysis of the potential effectiveness of different combinations of fuel, CIDI engine control strategies, and emission control devices on achieving emission reduction targets and engine and vehicle performance goals.

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C. Fuel Property Database

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This project also addresses the following DOE R&D Plan barriers and tasks:

Barriers

- A. Fuel Property Effects on Engine Emissions and Efficiency
- B. Fuel Property Effects on Exhaust Emission Control System Technology
- D. Sulfur Impacts
- E. Toxic Emissions
- F. Ultra-fine Particles

Tasks

- 2. Fuel & Lubricant Properties - Engine-Out Emissions
- 3. Fuel & Lubricant Properties - Exhaust Emission Control and Emissions
- 4. Develop Empirical Relationships

Objectives

- Establish and populate a web-based, searchable fuel property database for the Advanced Petroleum-Based Fuels (APBF) project which links to available emissions data.
- Utilize the database to develop empirical relationships between emissions and fuel properties.

Approach

- Define the fuel properties, engine and vehicle characteristics, and emissions to be included in the database.
- Build the database, web pages and appropriate web interfaces for the searchable database.

Accomplishments

- Searchable fuel property database completed and available on World Wide Web at <http://www.ott.doe.gov/fuelprops/>.
- Fuel property database linked to existing heavy vehicle emissions database.
- Several new fuels and over 150 emissions records added in the last year.
- Data in the database can be used to examine the trends in exhaust emissions over time.

Future Directions

- Continue to populate fuels and emissions databases as data become available.
- Complete expansion of the emissions database to include light-duty emissions data and engine emissions data, particularly from the APBF project.

Introduction

The effect of fuel properties, such as cetane number, aromatic content, and sulfur content, on exhaust emissions from diesel engines has been extensively studied. The use of alternative and advanced fuels (i.e. biodiesel, ultra-low sulfur diesel [ULSD], and Fischer-Tropsch diesel) in diesel engines and the resultant emissions effects have also been well documented. The impact of various fuel properties on diesel engines affects such systems as fuel injectors and exhaust aftertreatment devices. Thus, a detailed understanding of the influence of fuel properties is imperative to meeting future emissions targets without sacrificing operability and durability.

The APBF project studies a variety of fuels and fuel components and their impacts on exhaust emissions. The Liquid Fuel Property Database provides a single location for archiving data on fuels used in support of APBF research projects. The database is utilized to compare fuels, determine the effect of fuel properties on exhaust emissions, and investigate changes in exhaust emissions over time.

Approach

Heavy vehicle chassis emissions data is collected by West Virginia University (WVU) in support of the Department of Energy National Renewable Energy Laboratory (NREL) Truck and Bus Evaluation projects. The chassis emissions data is stored in a separate database maintained by NREL's Alternative Fuel Data Center. Results from this database are useful for examining trends in diesel emissions and comparisons of diesel and alternative fuel emissions [1-3]. Previous projects have often included a detailed fuel analysis and this analysis is required for all future projects. The results of these fuel analyses are archived in the Liquid Fuel Property Database, a web-based listing of fuels used in APBF research projects. Users can search the database and generate search results that can be imported into common desktop software projects for further analysis.



Figure 1. Fuel Property Database Selection Page, Includes Pull-Down Lists of Fuels and Properties

Results

The Fuel Property Database includes various chemical, physical, and operability property data, in addition to environmental health and safety information. The database is accessible at <http://www.ott.doe.gov/fuelprops/>. The main users of the database are technical experts involved in diesel fuel and emissions research.

The database is designed to allow the user to tailor a search to their need by selecting from a list of fuels and properties (Figure 1). The database allows the user to select one or more fuels and associated properties from these lists. The user can select SI or English units for the fuel properties. Optional display fields include the test method used in the analysis, the literature reference for the fuel, and a brief description of the fuel. An alphabetical glossary of the key terms is included to facilitate use of the database by novice users (Figure 2).

The database is linked to chassis emissions provided in support of the NREL Truck and Bus Evaluation projects. The user can select from a list of fuels and the database returns the chassis emissions data for that fuel (Figure 3). The search results provide information on the vehicle and engine (i.e.

Liquid Fuels Database Glossary



Figure 2. Glossary with Short Descriptions of Test Methods Referenced in Database Search Page

model year, type of vehicle, engine manufacturer, aftertreatment), chassis test cycle, the date the testing was performed, and the emissions results for the testing.

The chassis emission data in the Fuel Property Database can be utilized to determine the deterioration of emissions over time. For example, the emissions control diesel fuel (EC-Diesel) project is a government-industry project to evaluate the use of ULSD and diesel particle filters in several diesel fleets in the southern California area. Emission testing in the EC-Diesel project was conducted by WVU at the start of the project and twelve months later, at the completion of the project. Fuel analyses were performed for the fuels used in the project and are available in the Fuel Property Database. The associated emissions data can be used to examine the particulate matter (PM) emission deterioration over the twelve-month project for a subset of vehicles.

Five Ralphs grocery vehicles were operated on California Air Resources Board (CARB) diesel fuel for the duration of the EC-Diesel project. Emissions test results were extracted from the Fuel Property Database and analyzed. Table 1 shows the PM emissions results at the start and end of the test project for these five vehicles. Over the twelve-month period, the PM emissions increased by a factor of two, showing significant deterioration as a function of time.

The fuel properties from the CARB diesel can be extracted from the database to determine if a significant change in fuel properties may be

TEST YEAR	APDF-EM-CARB-COPYR	APDF-EM-CARB-1-Name	APDF-EM-CARB-COPYR
TEST CYCLE	C25F9	F-2500	C25F9
DESCRIPTION	40000	40000	40000
TEST DATE	01-MAY-2001	16-SEP-2001	01-APR-2001
APDF	0.20000	0.20000	0.20000
CO	0.00000	0.00000	0.00000
HC	0.00000	0.00000	0.00000
NOX	0.00000	0.00000	0.00000
PM	0.00000	0.00000	0.00000
CO2	0.00000	0.00000	0.00000
HCN			
CHCN			
Chassis Name	Test 1	Test 2	Test 3
VEH TYPE	CARB Diesel Engine B2E	CARB Diesel Engine B2E	CARB Diesel Engine B2E
VEH MANUFACTURER	Freight	Freight	Freight
VEH MAKE	Freight	Freight	Freight
VEH MODEL YEAR	2000	2001	2000
GVW	40000	40000	40000
EMG TEST	Common	Common	Common
EMG MODEL	M11-150-B20	M11-150-B20	M11-150-B20

Figure 3. Search Results of Chassis Emissions Data Page

responsible for the change in PM emissions. Table 2 compares the CARB diesel fuel used for emission testing at the start and end of the EC-Diesel project. No significant property changes were recorded, indicating that the change in PM emissions is not a result of changing fuel properties throughout the project.

Conclusions

The Fuel Property Database provides a single location for properties of fuels used in support of APBF research projects. Fuel properties are archived in a user-friendly, web searchable database. In addition to fuel property information, the Fuel Property Database contains chassis emission data from heavy-duty vehicles using many of the fuels in the database, including vehicle and engine configurations, test cycles, test date, and regulated emissions results. The Fuel Property Database provides a single site with voluminous information on diesel fuels and chassis emissions data associated with these fuels and will continue to be a valuable resource in support of APBF projects.

Vehicle	Date (Round 1)	PM, g/mi (Round 2)	Date (Round 2)	PM, g/mi (Round 2)
5915	2/11/2000	0.199	2/13/2001	0.368
5917	1/19/2000	0.146	2/16/2001	0.39
5918	3/9/2000	0.24	3/22/2001	0.66
5919	1/17/2000	0.208	3/27/2001	0.555
5920	1/15/2000	0.192	3/26/2001	0.555

Table 2. Fuel Properties for CARB Diesel Fuel Used in the EC-Diesel Project

Property	ASTM Test Method	Units	CARB Diesel Fuel Projections	
			Initial Testing	Final Testing
Density	D4052	kg/m ³	844.5	843.17
API Gravity	D27	°API	36	36
Distillation (IBP)	D86	°C	177.6	184.1
Distillation (50%)	D86	°C	274.1	269.5
Distillation (90%)	D86	°C	328.2	328.4
Distillation (EP)	D86	°C	351.6	351.4
Cetane Number	D613	--	54.1	51.4
Sulfur	D5453	ppm	121.1	114.5
Olefins	D1319	vol %	3.4	1.7
Saturates	D1319	vol %	72.8	78.3
Aromatics	D1319	vol %	23.8	20
Total Aromatics	D5186	wt %	22.5	16.1
Polyaromatics	D5186	wt %	4.1	3.78
Heat of Combustion (*HHV)	D240	MJ/kg	45.74	45.64
Heat of Combustion (*LHV)	D240	MJ/kg	42.89	42.76
Flashpoint	D93	°C	71.7	70
Cloud Point	D2500	°C	-9	-12
Pour Point	D97	°C	-12	-15
*HHV = Higher Heating Value *LHV = Lower Heating Value				

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D. Isotopic Tracing of Fuel Components in Emissions from Diesel Engines Using Accelerator Mass Spectrometry

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This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

A. Fuel Processing Effects on Engine Emissions and Efficiency

Tasks

2. Fuel & Lubrication Properties - Engine-Out Emissions

Objectives

- Determine contribution of specific carbon atoms in fuel components and oxygenates to certain emission products.
- Separate volatile and non-volatile fractions of soot.
- Test the effects of fuel molecular structure on combustion product distribution.
- Produce data to validate combustion modeling.

Approach

- Selectively label specific carbon atoms in dibutyl maleate to achieve a carbon-14 (^{14}C) contemporary fuel.
- Analyze carbon isotope content of all fuel components and lubrication oil.
- Collect soot and combustion gas from skip fired 1.7 liter optical engine. Complete isotopic analyses of soot and determine contributions from available carbon sources.

Accomplishments

- Reconfigured filter assembly and gas collection to improve throughput and cleaning of system.
- Completed preliminary tests to determine engine operation conditions for loading filters with sufficient soot for isotopic analyses.

- Reduced and nearly eliminated lubrication oil leakage as contributor of carbon emissions from test engine.
- Completed experiments tracing the fate of different maleate-derived carbon atoms from dibutyl maleate fuel to emissions products.

Future Directions

- Determine contributions of major fuel components to soot production and test selected oxygenates (e.g., tripropylene-glycol monomethyl ether).
- Apply tracing technique to measure contribution of aromatics and cyclo-alkanes to emission products in diesel engines.
- Collect gaseous emissions and separate major components.
- Obtain carbon-14 labeled lube oil and run it in a conventional diesel engine. Determine contribution of lube oil to soot and carbon dioxide (CO₂) emissions.
- Apply tracing techniques to homogeneously charged compression ignition engines.

Introduction

Accelerator mass spectrometry (AMS) is an isotope-ratio measurement technique developed in the late 1970s for tracing long-lived radioisotopes (e.g., ¹⁴C half life = 5760 y). The technique counts individual nuclei rather than waiting for their radioactive decay, allowing measurement of more than 100 low-level ¹⁴C samples per day (Vogel et al, 1995; Buchholz et al, 2002).

The contemporary quantity of ¹⁴C in living things (¹⁴C/C = 1.2x10⁻¹² or 110 femtomole [fmol] ¹⁴C/ g C) is highly elevated compared to the quantity of ¹⁴C in petroleum-derived products. This isotopic elevation is sufficient to trace the fate of bio-derived fuel components in the emissions of an engine without the use of radioactive materials. Another approach is to purchase ¹⁴C-labeled material (e.g., dibutyl maleate (DBM)) and dilute it with petroleum-derived material to yield a ¹⁴C concentration similar to a bio-derived fuel. In each case, the virtual absence of ¹⁴C in petroleum based fuels gives a very low ¹⁴C background that makes this approach to tracing fuel components practical.

Regulatory pressure to significantly reduce the particulate emissions from diesel engines is driving research into understanding mechanisms of soot formation. If mechanisms are understood, then combustion modeling can be used to evaluate possible changes in fuel formulation and suggest

possible fuel components that can improve combustion and reduce particulate matter (PM) emissions. The combustion paradigm assumes that large molecules break down into small components and then build up again during soot formation. AMS allows us to label specific carbon atoms in fuel components, including oxygenates, trace the carbon atoms, and directly measure how fuel molecular structure affects emissions.

Volatile and non-volatile organic fractions (VOF, NVOF) in the PM can be further separated. The VOF of the PM can be oxidized with catalysts in the exhaust stream to further decrease PM. The effectiveness of exhaust stream catalysts to oxidize products from tracer fuel components can be monitored through AMS measurement of carbon in PM.

Approach

The ¹⁴C concentration of all fuel components and the lubrication oil were checked by AMS and confirmed to be of petroleum origin (¹⁴C/C ratios ~10⁻¹⁵). Test fuels containing 88% DBM, 7% n-hexadecane (NHD) and 5% ethylhexyl nitrate (EHN) were spiked with DBM containing ¹⁴C labels in different positions in the molecule to obtain fuel containing 80-90 fmol ¹⁴C/ g C, approximately 70-80% the ¹⁴C found in living things (see Figure 1). The high concentration of DBM in the fuel was selected to study the combustion of the oxygenated

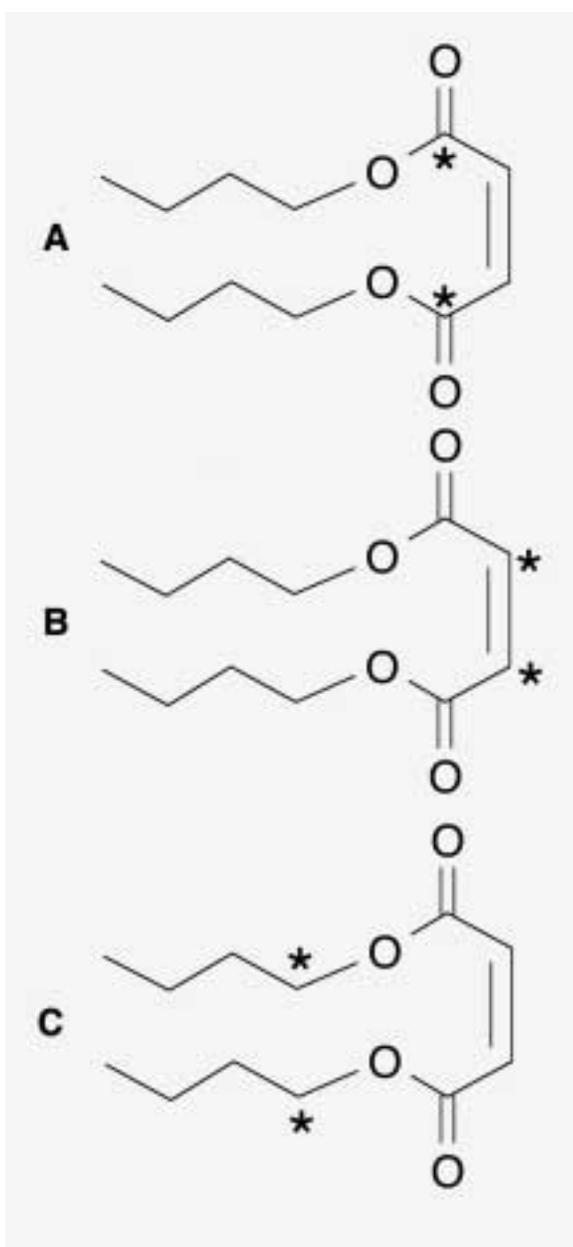


Figure 1. Dibutyl maleate molecule with the different labeled carbon positions indicated with asterisks: A) 1,4 maleate, B) 2,3 maleate, and C) 1-butyl. The symmetry of the molecule yields two chemically identical carbon atoms for each label.

hydrocarbon without the complication of high dilution in a conventional diesel fuel. Although the optical features of the engine are not discussed here, combustion of this fuel blend has been examined in detail at the Sandia National Laboratory (Mueller and Martin, 2002; Mueller, 2002).

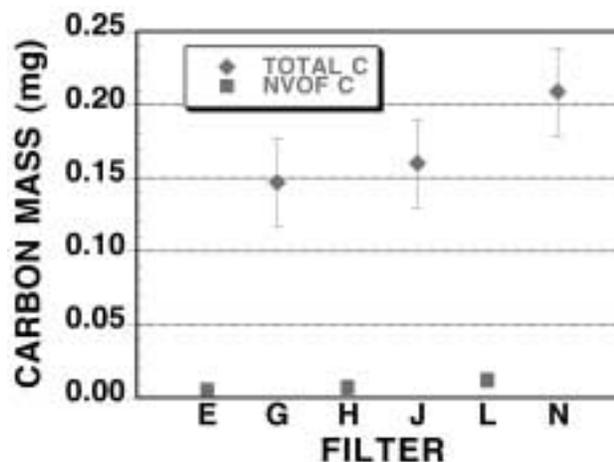


Figure 2. Mass of carbon deposited on motored only filters. Heating Filters E, H, and L to 320°C for 2 hours removed almost all carbon deposited from lube oil. Analyzing the total carbon on filters G, J, and N indicated that significant ^{14}C -free carbon was deposited on filters during motored runs.

Pre-combusted quartz filters were loaded with PM drawn from the exhaust manifold of a modern-technology, 4-stroke, heavy-duty direct injection (DI) diesel engine that has been modified to provide extensive optical access into the combustion chamber. Injection timing was optimized such that the engine produced maximum gross indicated torque. The engine operated at 1200-revolutions per minute and moderate load (8.00 bar gross indicated mean effective pressure). Typical optical engine runs in skip fire mode (fire every 12th cycle) utilized 48-84 fires to deposit sufficient soot for isotopic analysis.

Some filters were baked at 320°C for 2 hours to remove the VOF soot and unburned lubrication oil deposited on the filters during non-fired cycles. The remaining carbon on the filters was assumed to be NVOF. The procedure was developed using National Institute of Standards and Technology standard reference material 2975 diesel soot to obtain consistent isotope ratios and mass fraction of the NVOF. Switching to a poly-isobutylene based lubrication oil that cracks to butylene below 300°C has significantly improved removal of unburned lube oil from filters (see Figure 2). Improvements in the oil control system of the engine have also decreased oil deposition and improved operations.

Results

The ^{14}C content of NVOF soot varied significantly with the position of the label within the DBM molecule (Figure 3). Virtually no ^{14}C appeared in the soot when the label was placed in the 1,4 maleate position (double bond to an oxygen atom and single bond to another oxygen participating in the butyl ester structure [Figure 1a]). The 1,4 maleate carbon is completely converted to CO_2 . It is safe to assume that the carbon=carbon ($\text{C}=\text{C}$) bond survives combustion. The partitioning of the oxygen in the ester bridge between the 1,4 maleate carbon or the 1-butyl carbon will be determined in the coming months.

DBM with the ^{14}C label in the 2,3 maleate position (carbon-carbon double bond (Figure 1b)) produced soot with the same isotopic content as the fuel (Figure 3). Molecular fragments with carbon-carbon double bonds are known soot building blocks (Curran, et al., 2001; Westbrook, 2002). The NHD, EHN, and butyl groups in DBM are primarily n-alkane structures and likely to combust as typical diesel fuel.

Conclusions

Selective labeling of specific carbon atoms in a fuel component allows examination of the molecular structure effects on the combustion process. It is clear that nearest neighbor atoms in DBM influence the formation of molecular fragments. The data collected here provide direct validation of chemical kinetic models. Completion of the [1-butyl ^{14}C] DBM runs will likely produce soot with a ^{14}C content between the two maleates, providing information on partitioning of the oxygen in the ester bridge in DBM. Data are applicable to fuel design and provide information on the types of fuel structures that best reduce formation of PM.

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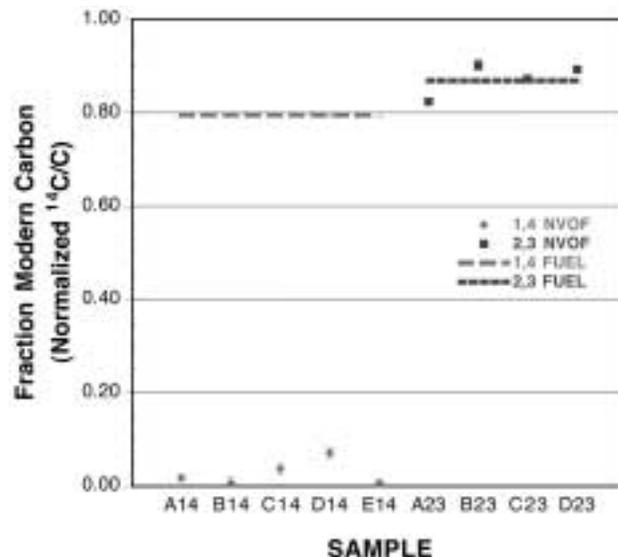


Figure 3. Concentration of ^{14}C in fuel and NVOF soot collected from [1,4 maleate ^{14}C] DBM (Figure 1A) and [2,3 maleate ^{14}C] DBM (Figure 1B). The NVOF soot collected with the 1,4 maleate label was essentially ^{14}C free while the 2,3 maleate label produced soot with the isotope content of the fuel.

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E. Performance and Properties of Renewable Diesel Fuels

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Main Subcontractors and Industrial Partners: AAE Technologies, Inc., Arlington, Virginia, Pure Energy Corporation, Paramus, New Jersey, Southwest Research Institute, San Antonio, Texas

This project addresses the following DOE R&D Plan barriers and tasks:

Barriers

- A. Fuel Property Effects on Engine Emissions and Efficiency

Tasks

1. Screening
2. Fuel & Lubricant Properties - Engine-Pit Emissions

Objectives

- Develop a multi-year plan for research & development (R&D) to overcome technical barriers to increased utilization of renewable fuels blended into advanced petroleum-based fuels
- Conduct an assessment of technical barriers to increased ethanol use in diesel, including acquisition of fuel property, emissions, and performance data
- Perform an analysis of the potential for using ethanol as a feedstock for producing more desirable diesel blending components
- Identify other potential renewable diesel blending components that could be produced from agricultural and waste products

Approach

- Analyze the potential for diesel fuel produced from renewable resources to displace petroleum diesel
- Acquire data on the performance properties of renewable fuels blended with petroleum-based fuels
- Measure emissions and stability for ethanol-diesel blends
- Review literature and information provided by stakeholders on performance of ethanol-diesel blends, ethanol conversion chemistry, technical status of biodiesel, and potential for additional renewable diesel options

Accomplishments

- Prepared a strategic plan for renewable diesel development
- Identified ethyl levulinate as a potentially high-quality, low-cost renewable diesel blending component
- Collected fuel property data for blends of ethanol, biodiesel, and ethyl levulinate with conventional and ultra-low sulfur diesel
- Assessed the technical barriers to use and commercialization of ethanol-diesel blends and issued a summary report
- Completed an analysis of renewable diesel blending components that could be prepared using ethanol as a feedstock
- Prepared a multi-year plan for R&D of renewable diesel blending components, based on a common fuel development pathway

Future Directions

- Investigate the causes of increased oxides of nitrogen (NO_x) emissions from biodiesel using in-cylinder pressure measurements and instrumented injectors
- Understand how to ensure biodiesel oxidative stability
- Perform R&D to address fuel injection equipment manufacturer issues with biodiesel
- Determine measures required to address the flammability hazards posed by the reduced flash point and increased vapor pressure of ethanol-diesel blends
- Obtain more detailed emissions data on ethanol-diesel blends, including emissions of toxic compounds
- Perform more detailed studies of fuel-engine interaction and fuel properties for ethyl levulinate blends with diesel fuel
- Assess R&D needs for Fischer-Tropsch (FT)-diesel derived from biomass

Introduction

Development of renewable diesel blending components is desirable in order to displace imported petroleum and to reduce emissions of global warming gases. Many of these fuels contain oxygen and therefore offer particulate matter (PM) emission reduction benefits for diesel vehicles, relative to conventional diesel. This project covers the development of strategic and R&D plans for renewable diesel fuels, along with assessments of the current technical status of these fuels. The results of these assessments along with fuel property data and the most important aspects of the R&D plan are discussed below.

A strategic plan for renewable diesel development was prepared that identified biodiesel and renewable-based FT diesel as the highest priority renewable diesel fuels. These fuels are strategic because of their potential to displace billions of gallons of imported petroleum diesel and the high

level of development of these technologies both in terms of fuel production and fuel use. Ethanol diesel blends are also important but have a much smaller petroleum displacement potential. Other fuels are at a basic R&D level but may have the potential to become strategic in the near to medium term. Longer term R&D should be directed at renewable fuels for advanced combustion concepts such as homogeneous charge compression ignition.

Approach

Information was collected from a variety of sources and evaluated to assess the technical status of renewable diesel fuels. Fuel property data, including American Society for Testing and Materials (ASTM) D975 properties as well as additional cold flow, lubricity, and vapor pressure properties were acquired under a subcontract with Southwest Research Institute. Data on ethanol-diesel emissions and blend formulation were obtained under a subcontract with Pure Energy Corporation (PEC).

Results

Biodiesel

Biodiesel is produced from various agricultural and waste fats and oils and consists of the methyl esters of fatty acids. Biodiesel is typically used as a 20% blend in conventional diesel but lower blending levels have recently been considered. Consequently several low biodiesel content blends were examined. It was found that 2% biodiesel could improve the lubricity of conventional and ultra-low sulfur diesels (scuffing load ball on cylinder lubricity evaluator [SLBOCLE]>4000 grams and high frequency reciprocating rig [HFRR]<0.25 millimeter), while up to 4% biodiesel had no impact on cloud point, pour point, or cold filter plugging point. Previous studies suggest that there is no measurable change in emissions for biodiesel blends at these levels. Fuel utilization R&D issues remain for biodiesel including:

- Cause and abatement of increased NO_x emissions at higher blend levels
- Understanding and ensuring oxidative stability
- Ensuring compatibility with fuel injection equipment at higher blend levels

Ethanol-Diesel Blends

More recently there has been interest in blending ethanol into diesel fuel, so called "e-diesel". The limited solubility of ethanol requires the inclusion of cosolvent or microemulsifier additives for blend stability, especially in the presence of water. Cetane enhancing additives are also required because of the low cetane number of ethanol. Ethanol also imparts a low flashpoint to the diesel fuel, a fact that is likely to limit the market for this fuel. An assessment of the technical barriers to commercialization of e-diesel revealed that the main technical barriers are:

- Low flashpoint. E-diesel cannot be safely handled like conventional diesel but must be handled like gasoline. The fuel tank vapor space is also likely to be flammable. This may necessitate some modifications to storage and handling equipment, as well as vehicle fuel systems.

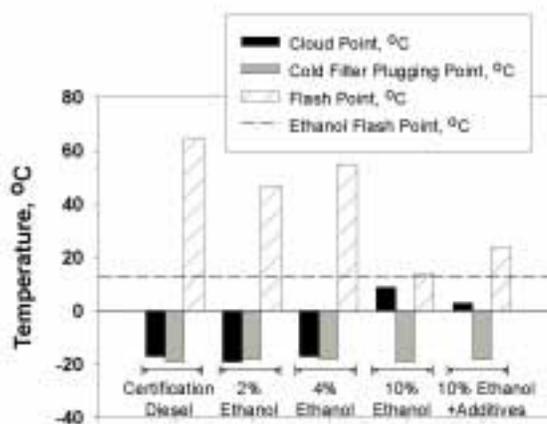


Figure 1. Results of Cloud Point (ASTM D2500), Cold Filter Plugging Point (ASTM D6371) and Flashpoint (ASTM D93) Determination for Various Ethanol-Diesel Blends

- Obtaining engine original equipment manufacturer warranty acceptance. At present engine manufacturers will not warrant their engines for use with e-diesel because of concerns about safety and liability, as well as materials and component incompatibility.
- Environmental Protection Agency (EPA) fuel registration requirements. As a non-baseline diesel fuel, e-diesel will be required to undergo Tier 1 and Tier 2 emission and health effects testing.
- Stability. The low temperature and storage stability of e-diesel, as well as water tolerance of these blends, needs to be quantified.

Figure 1 presents data on the cloud point, cold filter plugging point, and flash point of ethanol diesel blends. At 2 and 4 volume percent ethanol there was no change in cold flow properties and only a small depression in flash point. At these low blend levels the fuel blend behaves as a solution rather than as an emulsion. When 2000 parts per million (ppm) water, was added to the 2 and 4% blends, the cloud point increased to -5°C (not shown in figure). The fuel grade ethanol used for blending contained 4400 ppm water. Identical behavior was observed for 2% ethanol blended with an ultra-low sulfur diesel

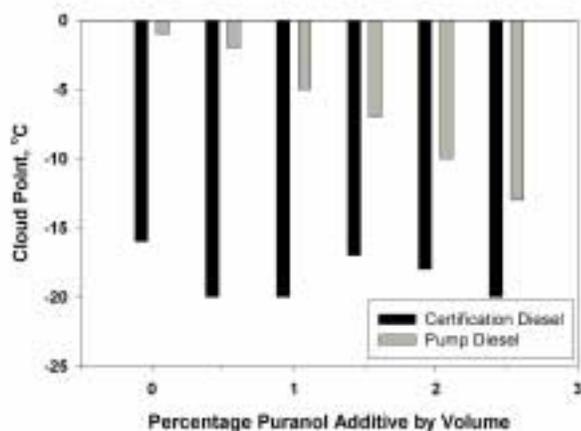


Figure 2. Cloud Point Data (ASTM D2500) for 10% Ethanol in Certification Diesel and a Pump Diesel at Various Additive Treat Rates

employed in the Advanced Petroleum Based Fuels-Diesel Emissions Control project. At 10% ethanol the flashpoint is essentially the same as that of denatured ethanol. The cloud point has increased to 9°C, but the cold filter plugging point is the same as that of the baseline diesel fuel. This indicates that the high cloud point is caused by the formation of liquid micelles large enough to be observed in the cloud point apparatus but still able to flow through a fuel filter. Addition of 0.6% of a commercial emulsifier additive package reduced cloud point for the 10% blend by 6°C and increased the flashpoint from 14 to 24°C. After addition of 2000 ppm of water, both 10% ethanol samples (with and without additives), exhibited phase separation at room temperature.

Testing performed by PEC has confirmed the impact of water on the stability of ethanol-diesel blends, showing room temperature phase separation for both 10 and 15% ethanol blended into a commercially obtained on-road pump diesel in the presence 1000 ppm water. Ongoing tests are examining the impact of PEC's Puranol additive on water tolerance. The PEC tests have also identified another stability related issue. Figure 2 shows cloud point data for 10% ethanol blended into a certification diesel and a pump diesel, including various percentages of their Puranol emulsifier additive. The certification diesel exhibits much lower cloud point (i.e. greater stability) than the

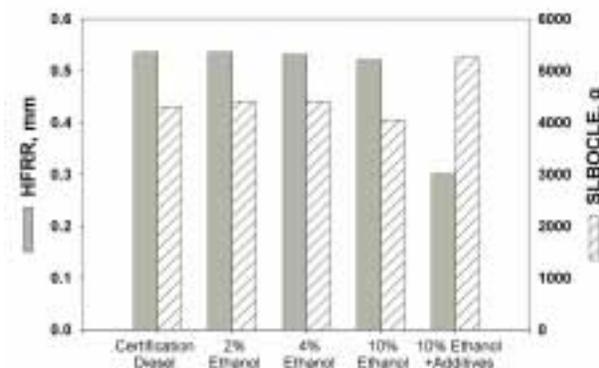


Figure 3. Lubricity results for various ethanol-diesel blends via HFRR (ASTM D6079) and SLBOCLE (ASTM D6078) tests

pump diesel at all Puranol treat rates. PEC believes that the pump diesel contains a number of additional additives including detergents, corrosion inhibitors, anti-microbial agents, and de-emulsifying agents added to repel water. These additives may inhibit the Puranol additives' ability to form a stable emulsion of ethanol in diesel. This suggests that successful production of e-diesel will require the use of un-additized diesel blending stock.

Figure 3 shows lubricity measurements for e-diesel samples via the HFRR and SLBOCLE methods. Addition of up to 10% ethanol had little impact on fuel lubricity, although the lubricity of the base certification diesel was not particularly high to begin with. Addition of 0.6% commercial emulsifier additive significantly improved the lubricity of the 10% ethanol blend (decreased HFRR and increased SLBOCLE).

Under the Clean Diesel III program at Southwest Research Institute (SwRI) in San Antonio, Texas, Pure Energy Corporation performed an engine test project using e-diesel. Within the Clean Diesel III Consortium, SwRI has developed an engine capable of co-injecting mixtures of water and diesel fuel with real-time control of the water percentage. In addition to this capability, the Real-Time Water Injection (RTWI) engine is equipped with a high-pressure loop exhaust gas recirculation (EGR) system featuring a variable geometry turbocharger. The SwRI and Pure Energy team performed a series of tests to investigate the potential benefits of water injection plus

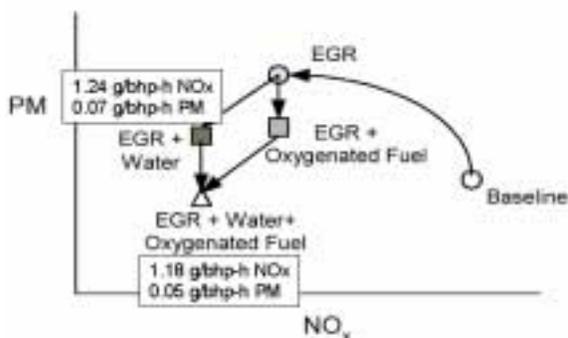


Figure 4. Qualitative Emission Reduction Pathway for E-Diesel Testing Under the SwRI Clean Diesel III Program

oxygenated fuel on emissions from the RTWI engine. The test fuels were a baseline diesel fuel and a 10% ethanol blend (containing the Puranol additive). Testing was conducted over the 13-mode steady-state cycle. The concept of using a combination of EGR, RTWI, and oxygenated fuel for reduction of NO_x and PM emissions is shown qualitatively in Figure 4. Application of EGR produces a reduction in NO_x from the baseline but a significant increase in PM. Injection of water causes a further reduction of NO_x and a reduction in PM. Use of oxygenated fuel reduces PM even farther. In this study, emissions of 1.18 g/brake horsepower-hour (bhp-hr) NO_x and 0.05 g/bhp-hr PM were obtained for the e-diesel blend using both EGR and RTWI. Water was injected at a rate equivalent to 30% of the mass of fuel consumed over the test. At the same engine settings (timing, EGR, etc.) and water injection rate the baseline diesel fuel (containing no ethanol) produced 1.24 g/bhp-hr NO_x and 0.07 g/bhp-hr PM. Thus in this test e-diesel produced a 5% reduction in NO_x and 29% reduction in PM. Changes in emissions are significant at 95% confidence.

The flashpoint and tank flammability issues for e-diesel are the top priority for future R&D. A further priority is obtaining emissions data on toxic compounds.

Oxygenates Produced from Ethanol

The flashpoint and stability issues evident for e-diesel have spurred interest in the potential of using ethanol as a feedstock for production of a higher

flashpoint renewable blending component. NREL has reviewed compounds that could be produced from ethanol along with a number of relevant fuel properties. Illustrative examples are shown in Table 1. Diethyl ether is easily prepared from ethanol by dehydration over an acid catalyst and exhibits a very high cetane number (Bailey, et al., 1997). However, the flashpoint of this material is so low that it could never be considered as a diesel blending component. Diethyl carbonate can be prepared from ethanol and carbon monoxide, is highly soluble in diesel fuel, but exhibits a low flashpoint and high corrosivity (Natarajan, et al., 2001). 2-ethoxy ethyl ether exhibits interesting fuel properties and is highly soluble in diesel fuel (Natarajan, et al., 2001); however, it has been shown to exhibit unacceptable toxicological properties (Forest, 1995). The final entry in Table 1, diethoxy butane, could be produced entirely from ethanol by dehydration to produce diethyl ether followed by oxidative coupling to produce the desired product. A second potential synthesis route employs petroleum derived butadiene, but even in this case 50% of the carbon content of the product is renewable. While flashpoint is slightly below the 52°C required for No. 2 diesel, blends with diesel may exhibit an acceptable flashpoint. Cetane number is also high. Other compounds with good fuel properties are ethyl esters of fatty acids and ethyl n-alkyl ethers.

Table 1. Properties of Ethanol and Potential Fuel Blending Components that Might Be Made from Ethanol

	Flashpoint °C	Cetane Number
Ethanol	13	8
Diethyl ether	-40	>150
Diethyl carbonate	25	--
2-Ethoxy ethyl ether	54	86
Diethoxy butane	45	97

Ethyl Levulinate (EL)

Cellulosic waste materials such as paper sludge, sawmill waste, silage, and unrecyclable paper can be converted to a chemical called levulinic acid (4-oxo-pentanoic acid) via a thermochemical conversion process. Cellulose is converted to levulinic acid with

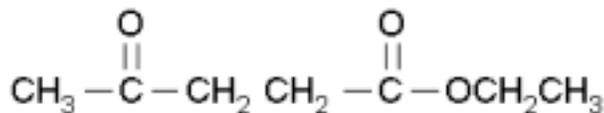


Figure 5. Structural Representation of Ethyl Levulinate

50% yield. Biofine, Inc. is developing this process with support from the New York State Energy Research and Development Authority and the DOE Office of Industrial Technologies, Forrest Products R&D program (Bozell, et al, 2000). Economic projections suggest that levulinic acid can be produced at a cost of from \$0.04 to \$0.10/lb. One use of levulinic acid is to produce ethyl levulinate (EL), the molecule shown in Figure 5. EL has been touted as a potential renewable diesel blending-component (Rohde, 2001). Given the high flash point of EL (91°C), the high lubricity imparted by the ester group, and the low projected cost of the starting material, measurement of the fuel properties of EL and EL-diesel blends were undertaken.

Some relevant properties of EL itself are listed in Table 2. The boiling point is in the normal diesel boiling range, and the high flashpoint indicates that the flammability problem that limits the market for e-diesel will not apply to this blending component. Heating value is on the order of 8,000 British Thermal Units/pound (btu/lb), lower than that of a conventional diesel fuel and on the order of the heating value of ethanol. However, the density of EL is 25% higher than that of ethanol, so that a given volume of this oxygenate contains significantly more energy. The cetane number of EL is low, indicating that a cetane-treating additive would also be required at higher blending levels.

Table 2. Properties of Ethyl Levulinate (Case No. 5339-88-8)	
Boiling Point, °C	206
Flashpoint, °C	91
Reid Vapor Pressure, psi	<0.01
Higher Heating Value, btu/lb	11241
Lower Heating Value, btu/lb	10459 (88692 btu/gal)
Density, g/ml	1.016 (8.48 lb/gal)
Cetane Number (IQT)	<10

EL was blended into certification diesel at 5 and 10 volume percent. Properties of these blends are listed in Table 3 and compared with those of the blending diesel certification fuel. At 5% and 10% EL there was no significant change in fuel properties with the exception of lubricity, which improved significantly. It is interesting to note that while the ignition quality testor (IQT) test predicts a cetane number of 5 for EL, the 5 and 10% EL blends exhibited no change, or even a small increase in cetane number as measured using ASTM D613. The results are encouraging for use of this material as a diesel blending component, but considerable additional data and testing are required. Specifically, it must be shown that EL-diesel blends are stable in the presence of water, and that EL is compatible with fuel system materials. Engine performance and emissions data are also required.

Table 3. Properties of Ethyl Levulinate-Certification Diesel Blends			
	Cert Fuel	5% EL	10% EL
Flashpoint, °C	65	76	77
Cetane Number	47	48	52
Cloud Number, °C	-17	-16	-14
Pour Point, °C	-18	-24	-18
Density, g/ml	0.8440	0.8541	0.8625
Viscosity, mm ² /s @ 40°C	2.610	2.527	2.470
Copper Corrosion	1A	1A	1B
SLBOCLE, g	4300	6000	5700
HFRR, mm	0.535	0.405	0.440

Future Directions

The R&D plan for renewable diesel fuels identified a common fuel development pathway consisting of the following steps:

- Safety and Environmental Impacts
- Blend Stability
- Fuel Performance Properties
- Material Compatibility and Pump Wear
- Engine Performance and Regulated Pollutant Emissions
- Toxic Compound Emissions (Tier 1 Testing)

- Engine Durability
- EPA Registration and Demonstration Studies

The fuel development pathway defines what R&D is needed for a given fuel based on its position in the pathway. The R&D plan also identified a number of issues critical to the expanded use of biodiesel, biomass-derived FT-diesel and to the commercialization of ethanol-diesel blends. Additionally, new renewable diesel blending components that could be produced from either ethanol or from cellulosic biomass have been identified.

For biodiesel future R&D will focus on development of a quantitative and fundamental understanding of both the increased NO_x emissions observed in many engines and oxidative instability of the fuel. An additional priority area for R&D is to understand the impact of biodiesel on fuel injection equipment performance, including materials compatibility and fuel pump durability. For ethanol-diesel blends the most important technical barriers are the low flashpoint of the fuel and the flammability of the tank vapor space. R&D to understand the measures that must be taken to safely use this fuel is being initiated late in fiscal year 2002 and will be ongoing in 2003. A second priority area for e-diesel is to understand the impact of this fuel on fuel injection equipment performance. Research to investigate issues associated with use of biomass derived FT-diesel and the performance of new renewable diesel oxygenates will also be initiated.

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4. McCormick, R.L., Alvarez, J.R., Graboski, M.S., Tyson, K.S., Vertin, K. "Fuel Additive and Blending Approaches to Reducing NO_x Emissions from Biodiesel" presented at National Biodiesel Board Research Brainstorming Meeting, January 23-24, 2002, New Orleans, LA.
5. McCormick, R.L. "Renewable Fuels Initiative" presented to NREL Fuels Utilization Program Task Leaders Meeting, February 26, 2002.
6. McCormick, R.L. "Technical Barriers to the Use of Ethanol in Diesel Fuel" invited presentation at 7th Annual National Ethanol Conference, February 27-March 1, 2002, San Diego, CA.
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ACRONYMS AND ABBREVIATIONS

ADMM15	15% by Volume DMM blended in ALS Fuel	EMA	Engine Manufacturers Association
ADVISOR	Advanced Vehicle Simulator	EPA	Environmental Protection Agency
ALS	Low Sulfur Diesel Fuel	FE	Fuel Economy
AMS	Accelerator Mass Spectrometry	FEERC	Fuels, Engines, and Emissions Research Center
ANOVA	Analysis of Variance	fmol	Femtomole
APBF	Advanced Petroleum Based Fuels	FT-100	Neat Fischer-Tropsch Fuel
APBF-DEC	Advanced Petroleum Based Fuels – Diesel Emissions Control	FTIR	Fourier Transform Infrared
API	American Petroleum Institute	FTP	Federal Test Procedure
ASTM	American Society for Testing and Materials	g	grams
ATDC	After Top Dead Center	g/mi	grams per mile
AVFL	Advanced Vehicle Fuel Lubricant	GC-MS	Gas Chromatography-Mass Spectrometer
bhp	brake horsepower	HC	Hydrocarbon
bhp-hr	brake horsepower-hour	HCCI	Homogeneous Charge Compression Ignition
BSFC	Brake Specific Fuel Consumption	HD	Heavy-Duty
btu	British Thermal Units	HSDI	High Speed Direct Injection
C	Carbon, Centigrade	HFET	Highway Fuel Economy Test
CA	California Reference Diesel Fuel	HFRR	High Frequency Reciprocating Rig
CARB	California Air Resources Board	hp	horsepower
CCV	Closed Crankcase Ventilation	hr	hour
CFFS	Consortium for Fossil Fuel Science	IMEP	Indicated Mean Effective Pressure
CH ₃ OH	Methanol	IQT	Ignition Quality Testor
CH ₄	Methane	LPP	Location of Peak Pressure
CIDI	Compression Ignition Direct Injection	LPPm	Location of Peak Pressure of Main Combustion
CO	Carbon Monoxide	MECA	Manufacturers of Emission Controls Association
CO ₂	Carbon Dioxide	Mo	Molybdenum
CVS	Constant Volume Sampler	MY	Model Year
DBM	Dibutyl Maleate	N ₂ O	Nitrous Oxide
DECSE	Diesel Emissions Control - Sulfur Effects	NH ₃	Ammonia
DF-2	EPA Certification Diesel Fuel	NHD	N-Hexadecane
DFI/GC	Direct Filter Injection/Gas Chromatology	Ni	Nickel
DI	Direct Injection	NO	Nitric Oxide
DMM	Dimethoxymethane	NO _x	Oxides of Nitrogen
DNPH	Dinitrophenylhydrazine	NREL	National Renewable Energy Laboratory
DOC	Diesel Oxidation Catalyst	NVOF	Non-Volatile Organic Fraction
DOE	Department of Energy	O	Oxygen
DPF	Diesel Particulate Filter	°C	degrees Celsius
EC-Diesel	Emissions Control Diesel fuel	ORNL	Oak Ridge National Laboratory
ECS	Emission Control System	PAH	Poly-cyclic Aromatic Hydrocarbon
EGR	Exhaust Gas Recirculation	PAS	Photoacoustic Analyzer
EHN	Ethylhexyl Nitrate	Pd	Palladium
EL	Ethyl Levulinate	PEC	Pure Energy Corporation

PM	Particulate Matter
ppm	parts per million
Pt/W/ZrO ₂	Platinum/Tungsten/Zirconium Dioxide
RPECS	SwRI Rapid Prototyping Electronic Control System
RTWI	Real-Time Water Injection
SCAQMD	South Coast Air Quality Management District
SCF	Supercritical Fluid
SCR	Selective Catalytic Reduction
SER	System Emissions Reduction
SLBOCLE	Scuffing Load Ball On Cylinder Lubricity Evaluator
SUV	Sports Utility Vehicle
SwRI	Southwest Research Institute
THC	Total Hydrocarbons
TPGME	Tripropylene Glycol Monomethyl Ether
ULSD	Ultra-Low Sulfur Diesel
US06	EPA Aggressive Driving Test Cycle
UV	Ultraviolet
VGR	Variable Geometry Turbine
VOF	Volatile Organic Fraction
WVU	West Virginia University
ZDDP	Zinc Dialkyl-Dithiophosphate